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THE DETERMINATION OF OPAQUE ORE-MINERALS BY X-RAY DIFFRACTION PATTERNS.

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INTRODUCTION.

THE merits of microscopic studies of ores are now well established and polished surfaces and thin sections are recognized as important auxiliaries that have helped to place economic geology upon a scientific basis. The laboratory methods, however, are still capable of much improvement, especially in one of the most fundamental tasks, mineral determination. Although in the majority of cases minerals can be determined fairly well by methods now in use, there are many instances in which the present means of approach are either cumbersome or inaccurate, and it is with these that we are at present concerned.

Mineral determination is so fundamental to economic geology that the existing methods may be examined in order to ascertain their limitations and possibility of improvement. A brief survey shows that the chief weaknesses lie in the determination of opaque ore-minerals rather than transparent minerals. This is especially true when ores contain rare minerals or even common ones in small amounts.

Physicists have developed X-ray analysis in recent years to such a point that the internal structure of any opaque crystalline substance can be determined from a pattern produced upon a photographic film due to the exposure of a small amount of a

powdered sample to a beam of X-rays. Since nearly all opaque minerals are crystalline this method is of use as a means of determination. It seems, therefore, that it should be possible to photograph diffraction patterns of known ore-minerals which could be measured and plotted on a chart to serve as standards for the identification of similar patterns that could be secured from unknown minerals. The method is accurate and if applicable should offer a solution of many problems in the determination of ore-minerals. It is the purpose of this paper to show some of the possibilities and limits of the powder method of X-ray analysis when applied to the diagnosis of opaque ore-minerals.

The problem was suggested by Dr. A. F. Rogers, Professor of Mineralogy at Stanford University, and the progress of the investigation has been greatly aided through his suggestions as well as assistance in securing mineral specimens. The writer also wishes to acknowledge an indebtedness to Professor C. F. Tolman, to Dr. D. L. Webster and Dr. P. A. Ross of the Department of Physics, and to Dr. O. L. Sponsler, who has been engaged in X-ray work upon starch. These men have given advice which has made possible comprehensive work upon a problem which involves mineralogy, economic geology, modern physics and X-ray technique.

PRESENT DETERMINATIVE METHODS.

Microscopes using reflected light for the study of opaque minerals have demonstrated their utility, but while they give information concerning the relations which exist between the various minerals shown on a polished surface, they are limited from the standpoint of determination. Tables of microchemical tests have been devised by Murdoch [1] and Davy and Farnham [2] for the identification of minerals by reflected light in an attempt to overcome these difficulties. These tests involve classification by

[1] Murdoch, J., "Microscopical Determination of the Opaque Minerals." New York, 1916.

[2] Davy, W. M., and Farnham, C. M., "Microscopic Examination of the Ore Minerals." New York, 1920.

means of visible chemical reactions which take place beneath the microscope, combined with tables of color, hardness and special characteristics. The tests are, however, subject to much variation due to impurities in the minerals. Furthermore, it is often impossible to find an area on a polished surface large enough for the application of a reagent to a single mineral, and when the testing solution covers two or more minerals at one time electrolytic action may take place and produce misleading results. Also, minerals often contain elements in solid solution, or isomorphism and polymorphism introduce additional difficulties. The color distinctions required by the determinative tables are often difficult. Because of these limitations the common minerals are frequently distinguished simply by their appearance in reflected light without recourse to other tests; but the determination of the rarer, although often important, minerals is still largely a matter of microscopic sight determination, particularly when they occur in small amounts.

Koenigsberger [3] realized the scarcity of information available for the accurate identification of minerals by reflected light and designed optical apparatus that would fit the polarizing microscope and enable one to obtain optical data for opaque minerals by the use of polarized reflected light. The essentials of this apparatus as stated in a condensed translation by Winchell,[4] consisted in the addition of a Savart plate, a plate of known refractive index, a reflecting prism and a contrast biplate of smoky quartz. The Savart plate is made up of two plates of calcite cut at 45° to the optic axis which are superimposed in such a way that the horizontal projection of the axis of one is at right angles to the axis of the other. The other units are introduced either for comparison effects or to direct and polarize the light. The Savart plate and mineral under examination combine to produce bands similar to those obtained with a quartz wedge between crossed nicols. The position of these bands varies for different

[3] Koenigsberger, *Centralblatt für Mineralogie, Geologie und Paläontologie*, 195–197, 1901; 565–568, 597–605, 1908; 245–250, 1909; 712–713, 1910.

[4] Winchell, N. H., and Winchell, A. N., "Elements of Optical Mineralogy," 1st ed., 1908.

minerals and Wright [5] has derived optical data sufficient for the determination of a number of opaque minerals based upon variations in the positions of the bands produced by different adjustments of the apparatus. It is evident, however, from a brief investigation of the method that while it may be a useful auxiliary it does not seem to possess the potential possibilities necessary for application to general determinative work. The information given is too meager and is not sufficiently distinctive. Furthermore, the optical data produce by no means as definite information regarding the mineral as may be secured from the study of an X-ray diffraction pattern.

No outline of determinative procedure is complete without a consideration of chemical and blowpipe analysis. While chemical and blowpipe work will always be important, yet, it is obviously inadequate for many of the finer distinctions required in the study of ores.

X-RAY ANALYSIS AS A DETERMINATIVE METHOD.

All methods of crystal analysis by X-rays depend upon the reflection [6] of X-ray waves from the planes of atoms in a crystalline substance. The fundamental assumption is made that crystalline substances are composed of atoms arranged in a space-lattice, while in an amorphous substance no such arrangment exists. Furthermore, crystalline substances reflect X-rays while amorphous substances do not.

From the standpoint of the reflecting medium there are three methods of X-ray analysis; 1, Laue's method, in which a beam of X-rays is passed through a thin oriented section of crystal; 2, the spectrometer method, in which X-rays are reflected from planes of atoms parallel to the smooth surface of an oriented crystal; 3, the powder method, where the rays pass through a small sample of crystalline powder.

The first method is named after the Swiss physicist Laue [7]

[5] Wright, F. E., *Proc. Am. Phil. Soc.*, 58, p. 401, 1919. *Min. and Met.*, No. 158, Sec. 9, Feb., 1920.

[6] The term reflection is not quite accurate but is sufficiently correct for purposes of general explanation and will be discussed later.

[7] Laue, M., *Ann. Physik.*, 41, 971–978, 989–1003, 1913.

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who established the fact that X-rays vibrate in the same way as light waves but with wave-lengths that assume atomic proportions. At his suggestion Friedrich and Knipping [8] placed oriented sections of a sphalerite crystal in the path of a small circular beam of X-rays. The crystal acted as a three-dimensional diffraction grating and the rays were reflected from the planes of atoms within the section at definite angles, as shown by the position of spots produced upon a photographic plate. These spots were arranged according to the symmetry of sphalerite as determined by external faces, with the exception of a center of symmetry which is not indicated by such photographs. The method has been developed and used in a large number of studies of crystal structure, and the atomic arrangements of crystalline substances that are in many cases opaque have been worked out in detail. It appears, however, that the use of the Laue method would be limited in determinative work because it requires oriented sections.

The spectrometer method was developed by the Braggs.[9] The X-ray spectrometer is analogous to the optical spectrometer aside from the fact that a smooth crystal face is substituted for the refracting prism and reflections are detected by means of an ionization chamber connected to an electroscope. The method requires the use of good-sized crystals with smooth faces that must be correctly oriented and hence is of little value from the standpoint of determination.

The third method, known as the powder method, was developed by Debye and Scherrer [10] and independently by Hull.[11] In crystal analysis by this method a sample of fine crystalline powder (.05 grams suffice) is placed in the path of a ribbon-like beam of X-rays. The powder causes reflections of the rays which are registered on a photographic film curved to form the arc of a circle with the sample at the center. The film shows a series of parallel lines of varying intensity and the pattern pro-

[8] Friedrich, W., and Knipping, P., *Ann. Physik.*, 41, 978–988, 1913.

[9] Bragg, W. H., and Bragg, W. L., "X-rays and Crystal Structure," 1st ed., London, 1915.

[10] Debye, P., and Scherrer, P., *Phys. Zeitschr.*, 17, 277–282, 1916.

[11] Hull, A. W., *Phys. Rev.*, 10, 661–696, 1917.

duced is characteristic of the crystalline material under investigation. Crystalline substances have an individuality of pattern which according to Hull [12] is distinctive. Opaque substances give results that are just as distinctive as those obtained from transparent substances as long as the material examined is crystalline and not amorphous.

Apparatus for taking powder photographs has been developed to such an extent that a standard diffraction outfit is now on the market that will analyze as many as thirty samples at one time. such an outfit described by Davey [13] of the General Electric Company may be operated for long periods with very little attention on the part of the operator. A water-cooled Coolidge tube is mounted with the axis vertical within a cylinder of heavy metal which protects the operator from the X-rays. Film holders which contain the samples to be analyzed, together with the recording film are arranged on the table around the cylinder. The exposures required are about 24 hours, but since thirty samples may be run at once the length of exposure is not an important factor. A high-tension transformer is beneath the table with high tension parts completely enclosed. The X-ray tube is cooled by a continuous flow of tap water.

This outfit is convenient and easily operated, so that, were it not for its high cost it would probably come into general use. The apparatus, however, is so expensive that in many laboratories it could not be seriously considered for determinative work. Therefore, because the powder method of crystal analysis seemed to offer a solution of some of the problems of mineral determination, an X-ray tube was secured and an outfit constructed in the laboratory which would be suitable for work with opaque ore-minerals.

DESCRIPTION OF APPARATUS.

The essential features of the apparatus [14] consist of a water-cooled Coolidge tube [15] with a molybdenum anticathode, and a

[12] Hull, A. W., *Phys. Rev.*, 17, 571–588, 1921.

[13] Davey, W. P., *Jour. Optical. Soc. Am.*, 5, Nov., 1921.

[14] The transformer and auxiliary electrical equipment used in this work was furnished through the courtesy of the Department of Physics.

[15] *Loc. cit.*

60-cycle alternating current transformer which is in reality an old induction coil taken from a discarded medical outfit. The tube is the standard water-cooled type that has been developed in the laboratories of the General Electric Company. It has a fine focus tungsten cathode and an anticathode consisting of a three-fourths inch copper pipe sealed at the end within the tube and capped with a small molybdenum button. While the tube is in operation a stream of water is kept circulating within the copper pipe in order to carry away the heat developed on the target.

The X-ray tube is mounted in a vertical position in the center of the table (Fig. 1) with the anticathode above. It is supported

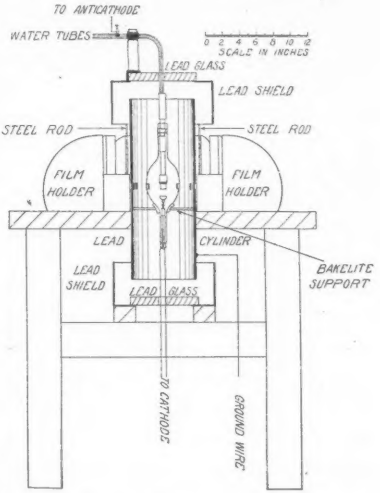

FIG. 1. Vertical section of diffraction outfit showing X-ray tube and arrangment of film holders.

at one end by bakelite and protected from jars by a small cushion of cotton that lies between the bakelite and the glass of the tube. The other end is held in place by a glass insulator that is fastened to the water pipes by means of sealing wax and tape. A cylinder of eighth-inch lead surrounds the tube and provides ample pro-

tection from X-rays. The open ends of the cylinder are covered with plate lead glass and shields of lead that provide ventilation without allowing X-rays to escape. Holes are drilled in the lead glass for the high tension wires and water tubes. Twelve equally spaced apertures are cut in the cylinder with their centers at 5° below the horizontal plane of the target. These openings permit the passage of the rays from the target of the tube to the slit system of a film holder. When any particular holder is not in place the opening is blocked with a piece of lead.

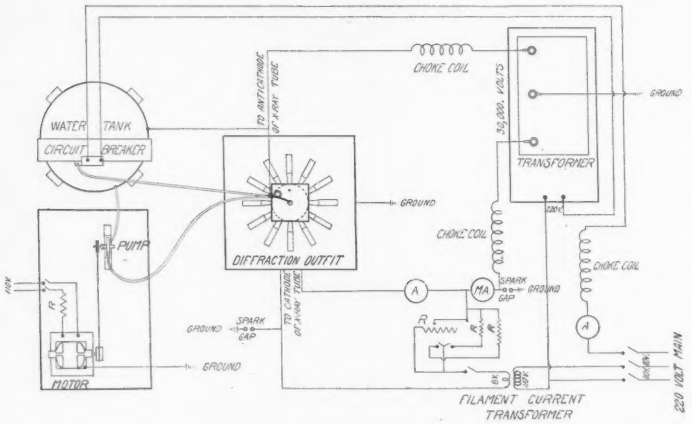

FIG. 2. Diagram of electrical connections and water-cooling system for diffraction outfit.

The transformer is of such a type that for long runs it is necessary to ground the middle of the secondary in order to protect the insulation. Therefore, the positive and negative ends must be insulated from the ground and since the water-cooling system is at the positive potential it must also be insulated. With more expensive transformers the positive end may be grounded and tap water connected directly to the X-ray tube. While the tube is in operation a constant flow of 1.5 gallons per minute is kept running through the anticathode and should the water flow

become impeded the current is turned off immediately by an automatic circuit-breaker. The water is stored in a 30 gallon tank and is circulated by a small centrifugal pump both of which are insulated by bakelite and glass, and the motor which drives the pump is connected by a leather belt.

A complete diagram of the electrical connections and water-cooling system is shown in Fig. 2. The electrical apparatus is arranged largely according to standard practice and it is hardly worth while to discuss in detail the wiring shown in the diagram. The voltage is measured by spark gaps and the only novel feature consists in a thread circuit-breaker [16] arranged for each spark gap. When an arc occurs a small thread stretched across the gap is burned and instantly releases an automatic device which opens a switch in the primary circuit of the transformer. These two devices together with the circuit-breaker in the water-cooling system make the outfit automatic in action and reduce the amount of attention required for its operation. The operating voltage is about 42 K. V. peak and the tube current is kept at about 30 milliamperes. In order to secure a tube current of 30 milliamperes the filament must be heated with a current of about 4.5 amperes.

Figure 3 shows sections of the type of film holder used. The function of a film holder is to limit the X-rays to a narrow beam that strikes the powdered substance and then registers the diffraction pattern produced upon a film which is placed along the arc of a circle with the sample at the center. The materials used in construction are lead, wood and sheet iron. One-sixteenth-inch lead is thick enough for all parts except the slit system where eighth-inch lead should be used because it is more rigid. The holder should be completely encased in lead and all cracks should be overlapped to prevent stray X-rays from entering and fogging the film. The two slits which define the beam are respectively .75 in. by .024 in. and 1.5 in. by .016 in. in size and are adjusted to produce as clear and sharp a line as possible upon the film. A third broad slit is placed between the two for the pur-

[16] A convenient piece of apparatus designed by Dr. P. A. Ross in connection with X-ray research and adopted in this work.

pose of halting stray rays and secondary radiation. The radius of the holder has been fixed at six inches because that distance seems to produce the best patterns in comparison to the time of exposure. Since the intensity of X-rays varies as the inverse

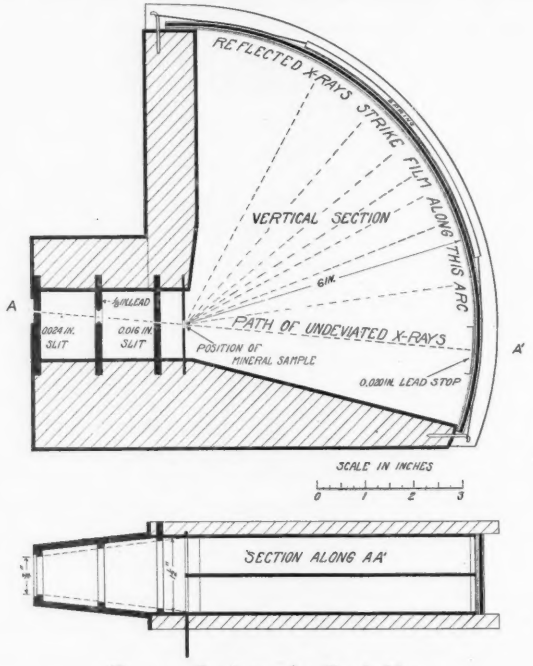

FIG. 3. Sections of a film holder.

square of the distance from the source it is advisable to make both the radius and the distance between the slits as short as possible. On the other hand, too much shortening is not advisable because the lines produced upon the film will become too closely spaced if the radius is reduced and will be blurred if the slits are too close together.

Each holder is divided into two compartments by a sheet of 1/16 in. lead so that two patterns may be obtained on the same

film. The powdered mineral is pressed into a rectangular hole cut in a strip of brass which slips into the film holder in such a way that there is a sample in each compartment directly in the path of the X-ray beam and exactly six inches from the film. A strip of .02 in. lead is placed at the back of the holder just in front of the film for the absorption of the undeviated beam until it is reduced to an intensity that will produce a clear image of the smaller slit. Eastman duplitized X-ray films are used and these are held in place by a lead strip strengthened with sheet iron that has been curved and lined with felt. This film back is held in position by a spring. Filters of aluminum, zircon or iron may be placed in front of the film to make the radiation nearly monochromatic or reduce the fogging due to short wave-lengths. Intensifying screens of calcium tungstate may be placed behind the film to reduce the length of exposure.

The cost of the diffraction outfit just described is probably not beyond the financial resources of the average university laboratory. The X-ray tube, of course, must be bought outright, but additional expenditures are dependent upon the amount of electrical equipment at hand and the number of units which must be purchased. It lacks some of the refinements of the standard outfits but will produce satisfactory pictures in about the same length of time and the conditions of operation are similar.

TECHNIQUE.

The mineral samples are ground until they will pass through a screen of china silk which should be free from filling and around 250 or 300 mesh. Samples that are not finely ground or carefully screened will produce spots and broken lines upon the film. The ground sample is pressed into the brass container. Ore-minerals are diluted with flour or some other light amorphous material before being pressed into the container because such small amounts are required that otherwise the sample would not have sufficient volume to stay in position. In some cases it is advisable to dispense with the flour and use glue or collodion. Light minerals such as quartz and calcite require no mounting material.

The density of the material and the extent to which it absorbs X-rays are the most important factors in determining the quantity of the sample to be used. Richtmeyer [17] gives a formula for the calculation of absorption coefficients and Hull [18] has derived an expression which will give the optimum thickness of sample for a given absorption coefficient. Thus it is possible to calculate the weight of a given mineral that should be used in order to get the most efficient reflections from X-rays. Such calculations, however, are at best only approximations. For this reason experimental data is often of more value in estimating the amount of a mineral that should be used than the computed optimum. Table I gives the weights of a number of minerals that have been found to produce diffraction patterns in grams per square centimeter of surface area exposed to X-rays.

TABLE I.

OPTIMUM WEIGHTS.

(Values determined from experimental data given in grams per square centimeter.)

Arsenopyrite ..... .08	Covellite ..... .08	Marcasite ..... .08
Bismuthinite ..... .04	Enargite ..... .05	Pyrrhotite ..... .06
Bornite ..... .05	Franklinite ..... .06	Pyrite ..... .08
Calcite ..... .25	Galena ..... .03	Quartz ..... .25
Cassiterite ..... .03	Goethite ..... .10	Sphalerite ..... .07
Chalcocite ..... .03	Halite ..... .20	Spinel ..... .10
Chalcopyrite ..... .05	Hematite ..... .08	Stibnite ..... .05
Chromite ..... .06	Ilmenite ..... .05	Tetrahedrite ..... .05
Cobaltite ..... .05	Magnetite ..... .07	

The length of exposure for a given sample varies inversely with the intensity of the X-rays given off by the target. When a voltage sufficient to produce lines has once been obtained the intensity of the radiation varies directly with the tube current. For this reason the tube current is kept around 30 milliamperes which is the maximum allowable. Under these conditions the heavy ore-minerals require exposures of from 10 to 24 hours, and light gangue minerals will give good patterns in from 6 to 12 hours.

[17] Richtmeyer, F. K., *Phys. Rev.*, 18, July, 1921.

[18] Hull, A. W., *Phys. Rev.*, 10, 1917.

Over exposure is a disadvantage because the field of the film becomes fogged and the diffraction lines are obscured.

X-RAYS AND FILTERS.

The principles which govern the propagation of X-rays and their application to this particular method of analysis may be considered in order to understand the type of radiation given off by the X-ray tube and the explanation of X-ray diffraction which follows.

X-rays are given off by the anticathode of a highly exhausted tube due to a bombardment by negative electrons from the heated filament of the cathode. In order to produce the stream of electrons and consequent flow of X-rays it is necessary to heat the filament to a white heat and maintain a high voltage. The rays travel in a manner similar to light waves but have exceedingly short wave-lengths that are smaller in most cases than the distances between atoms. The wave-length is dependent upon the material which makes up the anticathode and the radiation of any individual element is not monochromatic, but possesses a variety of wave-lengths, a few of which have such a high intensity as compared to the rest that when photographed in a spectrometer they appear as spectrum lines. The lines are developed in groups at different voltages and are designated as K, L and M-series. The M-series appears at the lowest voltage and contains the longest wave-lengths, while the K-series is made up of shorter wave-lengths and is produced at much higher voltages.

In the case of molybdenum (the target material employed in this work) the K-series waves have a moderate penetrating power and the L and M-series do not have a sufficient amount of penetrating power to be of any use in X-ray analysis of ore-minerals. In fact, M-series waves do not even penetrate the glass of the tube. The K-series is developed at 20 K.V. and increases in intensity as the voltage is raised. For work with diffraction patterns, however, the most desirable voltage is in the neighborhood of 28 to 30 K.V. rms. or about 40 to 45 K.V. peak. This voltage will produce the greatest contrast between

the characteristic radiation which produces the lines and the continuous radiation which fogs the film.

This K-series of molybdenum contains four distinct lines that are designated in the order of diminishing intensity as α_1, α_2, β and γ, and Duane[19] gives the following figures for their wave-lengths.

$\alpha_2 = .71212$ Å $\qquad \beta = .63110$ Å.
$\alpha_1 = .70783$ Å $\qquad \gamma = .6197$ Å.
(Å — Ångstrom Unit — $\times 10^{-8}$ cm.)

The two α-lines have nearly the same wave-length and when photographed by the spectrometer method produce two strong lines near together that are designated as the α-doublet. In such a photograph the β-line would appear a short distance away and γ would be a faint line near β on the opposite side from the two α-lines. α_1 is about twice as intense as α_2, and α_2 in turn is stronger than β, while γ is much weaker than the others. In reflections from crystalline powders α_1 and α_2 are so near together that they appear on the film as one strong line, while β is a weak line nearby, and γ is seldom observed.

It is often desirable in work with powdered minerals to secure a radiation in which even the smaller proportion of β-waves is absent. This is accomplished by the use of an absorption filter containing the element zirconium (either zircon or the oxide of zirconium may be used). It so happens that the K-series absorption limit for zirconium is .690 Å, which means that X-rays with wave-lengths slightly shorter than .690 Å will be highly absorbed while those a little longer will pass through with the minimum of absorption possible for the element.[20] Since the Kα-doublet of molybdenum has a wave-length slightly greater than .690 Å. It will pass through a thin sheet of zirconium with the minimum of absorption while shorter wave-lengths which include β will be highly absorbed. The effect of this is to produce a radiation composed almost entirely of α-waves. In practice a

[19] Duane, W., *Bull. Natl. Research Council*, Vol. 1, Part 6, No. 6, 1920.

[20] Kaye gives a comprehensive explanation of absorption which is beyond the scope of this paper. Kaye, G. W. C., "X-rays," 2d ed., London, 1923.

sheet of zircon or ZrO_2 which contains about .06 grams per square centimeter mounted in cellulose is placed directly in front of the film. Such a filter almost eliminates the β-lines and greatly reduces the general radiation which is composed of intermediate wave-lengths that tend to fog the films but do not produce lines. The use of a filter, however, causes a large increase in the length of exposure. In determinative work the β-lines are not always a disadvantage and reasonably clear pictures in which a few weak β-lines remain may be secured in less time by the use of sheet of .5 mm. aluminum. For this reason aluminum filters were used for the majority of the photographs in this work.

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DIFFRACTION OF X-RAYS.

Up to this time we have spoken of X-rays as being reflected, yet this term is not absolutely correct for the rays are not reflected from smooth surfaces as in the case of ordinary light, but suffer diffraction from internal planes of atoms. This involves the fundamental assumption that crystalline substances which diffract X-rays are composed of symmetrically arranged atoms which lie in planes, while in amorphous material no such arrangment exists and consequently there is no reflection. This assumption is well established by agreement with much experimental evidence. The next step is to consider what actually takes place when X-rays are diffracted.

A complete description of X-ray diffraction has been given by the Braggs[21] and the following discussion is modified in part from their text. Fig. 4 represents the cross-section of a crystalline substance normal to a set of parallel planes of atoms. The horizontal rows of dots represent parallel planes of atoms while the irregular line indicates the external surface of a crystalline substance. *I, I', I''*, etc., represent a train of advancing waves that will intersect the planes of atoms and *OR* is the emerging beam. The angle θ at which the rays strike the planes of atoms is the glancing angle. The distance between the planes of atoms is d and the wave-length of this train of X-ray waves is λ.

[21] Bragg, W. H., and Bragg, W. L., "X-rays and Crystal Structure," 1st ed., London, 1915.

The direction of reflection is determined by the same law of equal angles that holds in light and the wave-length remains the same after the rays emerge from the crystal. The total reflec-

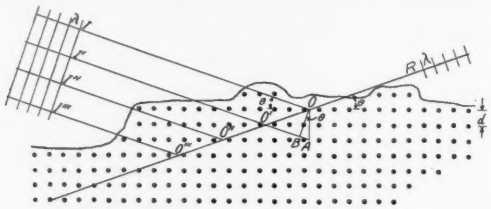


FIG. 4. Diffraction of X-rays from an oriented crystal.

tion from any one crystal face is a resultant of the reflections from all of the internal planes of atoms within the crystal parallel to that face. A single plane of atoms would produce a negligible effect. The number of coöperating planes necessary to produce a reflection is not definitely known, but from calculations based upon the thickness of crystals required to give good reflections and the diameters of their atoms determined by X-ray measurements, it may be shown to be very great (measured in millions). In order to produce reflections the waves reflected from each succeeding plane of atoms must be some integral multiple of λ behind the preceding one. When the angle θ is increased or diminished by such an amount as to make the difference in phase between two successive planes even as small as 1 in 2,000, the secondary waves will interfere in the strict sense of the word and no diffraction will result; the reason being that such a condition would cause the first plane to be nullified by plane 2,001, and in the same way all of the other reflections from the first 2,000 planes would be counteracted by the second 2,000 and so on. Thus the million or more planes necessary to build up a reflection would not reinforce each other.

From the above it may be seen that in the figure, IOR equals $I'O'R - \lambda$, and since OO' equals AO', λ is equal to AB. In the triangle ABO; $AB = 2d \sin \theta$. Substituting λ for AB;

$$\lambda = 2d \sin \theta,$$

where both d and λ are measured in Ångstrom units. If the angle at which the waves strike the planes of atoms is increased until the reflected waves differ in phase by 2, 3, 4 or more times, reflections are secured which are designated as second, third or fourth order and the equation for reflection is written,

$$n\,\lambda = 2d \sin \theta,$$

where n designates the order of reflection.

The exact structure of the atom has not been established, but it is generally considered that each atom consists of a positive nucleus surrounded by negative electrons. Upon exposure to X-rays, vibrations are set up within the atom. This vibratory mechanism produces secondary X-rays, and when the proper conditions of wave-length and spacing of the planes are satisfied, the waves emitted by the various planes of atoms will reinforce each other and "reflection" will occur.

DIFFRACTION FROM CRYSTALLINE POWDERS.

To understand the reflections that may occur from crystalline powders an idealized cross-section of a powdered mineral sample placed in the path of a fixed monochromatic beam of X-rays is

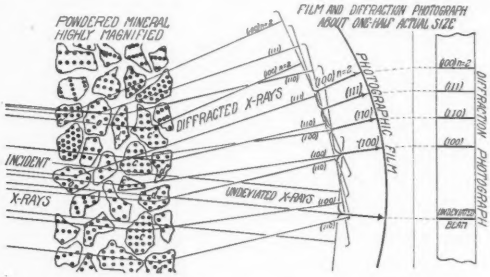


FIG. 5. Idealized representation of the diffraction of X-rays from a crystalline powder. (Atoms are magnified in much greater proportion than the outlines of the fragments.)

represented in Fig. 5. The fragments are irregular in outline and lie in all possible positions. The atomic planes are indicated

by dots and those fragments that happen to lie in a position to reflect X-rays are lettered according to the form represented; (c), (d), (o) and (c') indicating the cube, dodecahedron, octahedron and second order position of the cube respectively. The laws of diffraction which have been shown to apply to a single group of parellel planes of atoms apply to each of the crystalline fragments in the powder individually. Since the incident beam of rays is fixed, reflection will occur only from those crystals which lie in such a position that they satisfy the conditions of the equation $n\,\lambda = 2d \sin\theta$. The spacing d differs for the different types of atomic planes in the same crystalline material and λ remains the same so there will be a variation in the angle of reflection corresponding to changes in d.

As an illustration, take the case of galena in which the atoms are arranged at the vertices of a simple cube. The angles of reflection from the cube (100), dodecahedron (110) and octahedron (111) forms of galena are respectively, 6° 49′, 9° 37′ and 11° 33′. A second reflection occurs from the cube at 13° 57′ which satisfies the equation $2\,\lambda = 2d \sin\theta$ where d is the distance for (100). This reflection, consequently, is known as the second order of (100) and is designated (100) $n = 2$. All crystals in the powder that have (100) planes which make an angle of 6° 49′ with the beam of incident X-rays will reflect, and the combination of all the (100) planes which are correctly oriented will produce a cone of rays with the sides at an angle of $2\,\theta$ or 13° 38′ with the axis or undeviated beam. The same may be said for (110) and (111) but the angle will differ in each case. Since the relative spacing of the lines is all that is desired, a narrow strip of the film is sufficient to record the reflections, and in order that the arc $2\,\theta$ may be measured directly the film is curved to form the arc of a circle which has the powdered sample in the center.[22] In computing atomic spacings the arc is measured directly from the film, and since the radiation is monochromatic with a known wave-length, the distances between the planes

[22] The figure shows only those reflections which occur on one side of the undeviated beam, although a similar set could be photographed on the side opposite if the film should be extended.

of atoms may then be calculated in Ångstrom units by means of the equation given above.

COMPUTATION OF A DIFFRACTION PATTERN.

The use of the cube, dodecahedron and octahedron forms of galena in the preceding explanation of a diffraction pattern, while well supported by experimental evidence, is in fact theoretical. It is necessary, however, to understand the theory in order to have a better idea of the meaning of the lines in a pattern. So much information is contained in a single diffraction photograph that its real significance is overlooked unless at least a few pictures have been measured and computed.

The fundamental arrangments in all crystal structures are the fourteen space-lattices of Bravais.[23] From these space-lattices are derived the 230 space-groups of Schoenflies[24] which include all of the possible arrangments of points in space.[25] The theoretical spacing of any of the planes of atoms in a space-lattice may be computed in terms of assumed units. It is possible to measure the lines on any diffraction pattern, compute the atomic spacing, and by a process of comparison assign a crystal structure. This procedure is fairly simple for the isometric, hexagonal and tetragonal minerals but is complicated for those that occur in the other crystal systems.

A simple illustration of the computation of a diffraction pattern and the determination of a crystal structure is furnished by sodium chloride. Bragg has shown that the simple cube space-lattice should be assigned to sodium chloride, with the chlorine and sodium atoms arranged on alternate vertices. This substance gives good powder reflections and is used as a test sample to check the measurements of the film holders because of the simplicity of its crystal structure and the ease with which diffraction patterns may be obtained. The diffraction photograph

[23] Bravais, A., "Études Christallographiques." Paris, 1866.

[24] Schoenflies, A., "Krystallsysteme und Krystallstructur." Leipzig, 1891.

[25] Tutton gives a complete survey of this subject. Tutton, A. E. H., "Crystallography and Practical Crystal Measurement," Vol. I., 2d ed., London, 1922.

for sodium chloride is shown at the top of Plate I. Each line in the print measures an arc from the undeviated beam equal to 2θ in the formula $n\lambda = 2d \sin\theta$. Therefore,

$$\theta = \frac{360}{4\pi r} \times (\text{arc in mm.})$$

In the above expressions the spacing of the planes of atoms is the only unknown, since r the radius of the film holder may be easily measured (152.3 mm.), and it will be remembered from the discussion of the radiation given off by the molybdenum tube that the wave-length ($\lambda = .70783$ Å.) is fixed. Table II. gives a record of the computations of the planes of atoms for all of the forms of sodium chloride that register within 150 mm. of arc on the film, based upon the strongest α_1-line of molybdenum. The first column shows the spacing of the lines measured in millimeters of arc from the undeviated beam, the second the value of $\sin\theta$ for that arc, the third the computed spacing of the planes in Ångstrom units, the fourth the ratios between the planes assuming 2.817 Å. as unity based entirely upon measured distances, the fifth the theoretical ratios of the distances between the various planes of atoms in a simple cube where the distance between (100) planes has been assumed equal to unity, while the last column gives the Miller indices of the planes of atoms and states whether the reflections are of the first, second or higher orders. The fourth and fifth columns of figures check closely, and it is because of this close agreement between the theoretical and experimental ratios that it has been assumed that the atoms of sodium chloride are arranged on the corners of a simple cube and that their spacing is 2.817 Å. (the generally accepted figure is 2.814 Å.) from center to center. It has been shown by Bragg from properties of symmetry and from a study of the variations in the intensity of the lines in spectrometer studies that the Na and Cl atoms occur at alternate vertices of the structure.

Computations similar to the above could be applied to the diffraction pattern of any crystalline substance provided the proper space-group could be readily determined. Such computations,

however, do not materially increase the value of the diffraction patterns for determinative work and are beyond the scope of this paper.

TABLE II.

COMPUTATIONS FOR SODIUM CHLORIDE.

Experimental.				Theoretical.	
Arc in mm.	Sine θ.	d in Å. ($\times 10^{-8}$ cm).	Ratios if 2.817 = 1.00	Ratios for Simple Cube.	Indices of Form.
38.3	.1256	2.817	1.000	1.000	(100)
54.4	.1779	1.990	.707	.707	(110)
67.0	.2184	1.619	.575	.577	(111)
77.0	.2507	1.410	.500	.500	(100) $n = 2$
86.9	.2821	1.252	.446	.447	(210)
95.5	.3087	1.145	.407	.408	(211)
111.0	.3554	.995	.354	.354	(110) $n = 2$
118.0	.3784	.934	.332	.333	(221) or (100) $n = 3$
124.5	.3979	.889	.316	.316	(310)
131.0	.4173	.847	.301	.301	(311)
138.0	.4384	.807	.287	.288	(111) $n = 2$
143.7	.4555	.776	.276	.277	(320)
150.0	.4738	.747	.265	.267	(321)

One reason for including the tabulation for sodium chloride is to show the close check which exists between the ratios computed upon the basis of experimental evidence alone and those computed independently for the simple cube lattice. It emphasizes the precision attainable by this method of analysis. Any sample of sodium chloride should produce exactly the same results given above, because the figures are based upon atomic properties and arrangments which are the points that in the last analysis distinguish Na Cl as a distinct compound, and should they vary a different compound would result. As would be expected all samples of sodium chloride thus far known to have been tested have produced exactly the same diffraction lines.

STANDARD DIFFRACTION PATTERNS FOR THE DETERMINATION OF MINERALS.

The powder method offers two possible means of distinguishing minerals. The first is to proceed with the computation of a

diffraction pattern as in the case of sodium chloride and determine the actual spacing of the atoms in Ångstrom units: when this has been found, all of the possible arrangments of atoms characteristic of crystalline minerals previously determined or already on record in the literature[26] are investigated until one is located that will give planar distances corresponding to those obtained from the spacings that have been determined experimentally for the unknown. This procedure is accurate, but in dealing with orthorhombic, monoclinic and triclinic minerals would be tedious and hence impractical. The second method, which is the one adopted here, is to secure first the patterns of known minerals that may be used as standards and then distinguish unknown minerals by comparison with these standards. This procedure is simpler and seems better adapted to determinative work.

The ultimate aim of this study is the determination of rare minerals, but this necessitates first, a familiarity with the common minerals. A complete survey of all opaque minerals is beyond the scope of this paper, consequently, the results given must be considered as introductory to the diagnosis of minerals by the powder method and it is to be hoped that future work will produce results that will accomplish the desired end. Thus far all of the minerals examined have given distinctive patterns and except in a special case of isomorphism they may be easily distinguished from each other.

The method of reproducing the results of diffraction photographs in order to make them most useful to others must inevitably be open to discussion. The ideal procedure would be for all engaged in the work to have the original photographic negatives of the standard minerals and it is altogether likely that any laboratories that might decide to take up this work would photograph a series of their own standards. In all preliminary work, however, the probable limitations and advantages of the method should be known, and in order to show these the diffraction

[26] This is possible since crystal structure data obtained by the powder method has been shown by Hull to agree with that obtained by other methods of crystal analysis.

patterns of a number of common minerals are plotted to scale in Fig. 6. An enlarged chart of the same type in which the spac-

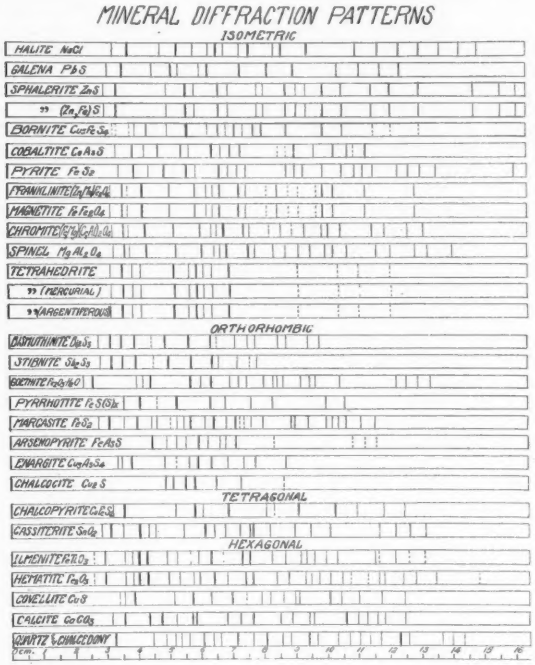


FIG. 6. Charted diffraction patterns. Both β and α-lines appear. Light lines represent weak α-lines and β-lines; very weak lines are dotted.

ings correspond exactly with those of the standard negatives has been found to be useful, especially, when working with mineral mixtures typical of ores. The plotted lines in the figure referred to may be measured in millimeters from the undeviated beam, which is indicated by zero on the scale, and this distance should be equal to twice the angle of reflection from the planes of atoms that caused the lines. Care was exercised to secure pure samples so that all of the lines could be definitely assigned to the min-

POSITIVE PRINTS OF MINERAL DIFFRACTION PATTERNS.

All photographs, unless otherwise indicated, were taken with a film holder having a 152.3 mm. radius, and a .5 mm. aluminum filter. The white line at the extreme left of each print indicates the position of the undeviated X-ray beam in the pattern. Prints are reproduced in natural size except for slight shrinkage which can be ascertained by reference to sodium chloride.

EXPLANATION FOR PLATE I.

No. 1. Sodium Chloride. Used for standardizing film holders. 10 hours.

No. 2. Galena. Galena has the same crystal structure as sodium chloride but the atomic volumes are larger and consequently the diffraction lines although similar are more closely spaced. 20 hrs.

No. 3. Sphalerite, rich in iron from Breitenbrunn, Saxony, 20 hrs.

No. 4. Pyrrhotite. 15 hrs.

No. 5. Pyrite. 15 hrs. Zircon filter.

No. 6. Marcasite. The orthorhombic form of FeS_2. Compare with pyrite (No. 4) the isometric form of FeS_2. 15 hrs. Radius 154.5 mm.

Spinel Group.

No. 7. Franklinite. This pattern is identical with that for magnetite (No. 8) 18 hrs.

No. 8. Magnetite. 18 hrs.

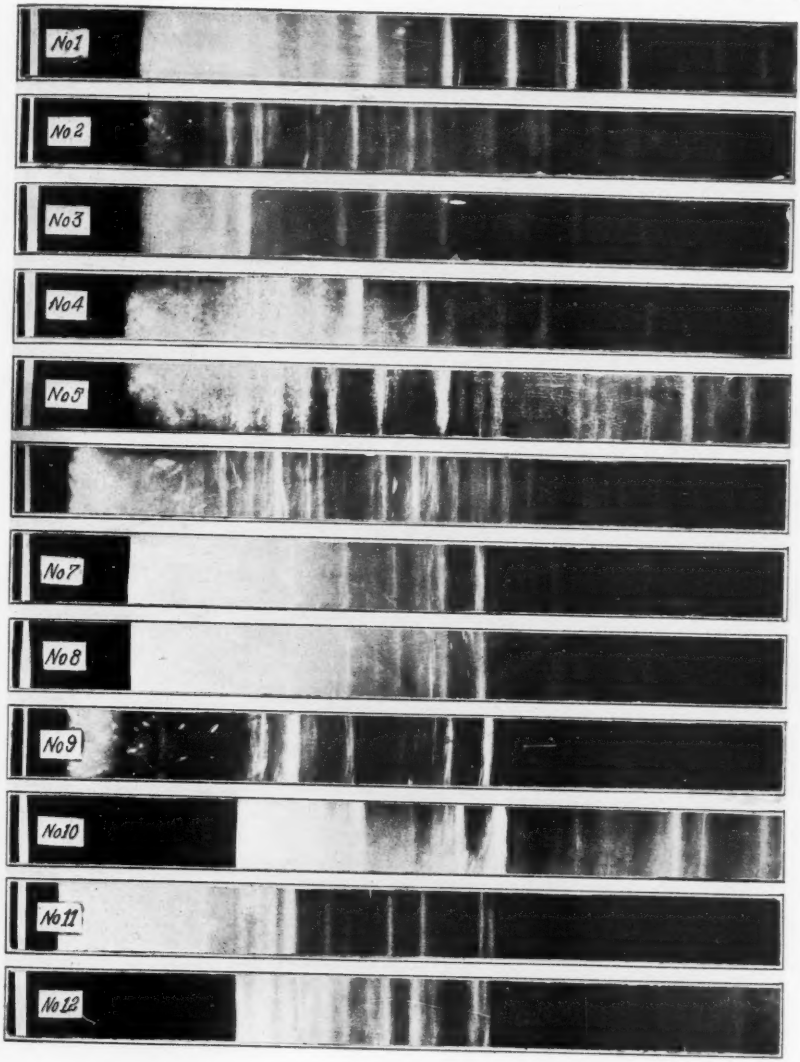
No. 9. Chromite. Note broader spacing due to smaller atomic volumes. 20 hrs. Radius 154.5 mm.

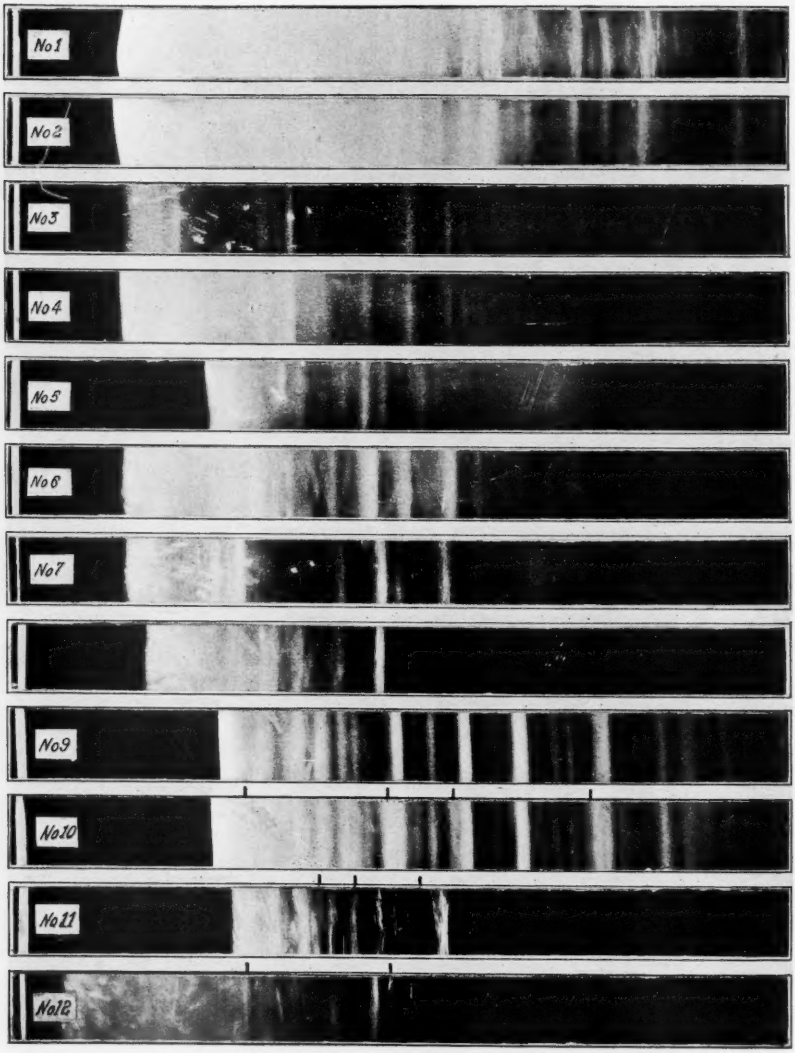
No. 10. Spinel. The spacing is still broader than that for chromite. Lines are more intense than those for the other members of the group because of a slight over exposure. 20 hrs.

Hematite Group.

No. 11. Hematite. Pencil ore. The clear lines are due to the finely crystalline condition of the powder. 15 hrs. Radius 154.5 mm.

No. 12. Ilmenite. Isomorphous with hematite and shows the same type of pattern with a slightly shorter spacing. 18 hrs.


No1
No2
No3
No4
No5
No7
No8
No9
No10
No11
No12


No1
No2
No3
No4
No5
No6
No7
No9
No10
No11
No12

EXPLANATION FOR PLATE II.

No. 1. Cassiterite. Tranparent Bolivian ore. Streaks are due to coarse particles in the powder. 20 hrs.

No. 2. Cassiterite. "Wood tin" from Cornwall. Sharper lines are produced in this sample of cassiterite than in the coarse crystalline variety shown above. 20 hrs.

No. 3. Goethite. 15 hrs.

No. 4. "Limonite." This particular specimen appeared dark between the crossed nicols of the polarizing microscope. 15 hrs.

No. 5. Chalcocite. 25 hrs.

No. 6. Covellite. 20 hrs.

No. 7. Chalcopyrite. 20 hrs.

No. 8. Bornite. Note the distinctive heavy line that stands out in the center of the pattern. 20 hrs. Radius 155.5 mm.

No. 9. Quartz. (Variety chalcedony.) Chalcedony gave smoother lines than those obtained for quartz although the two patterns are identical in spacing and variation of intensity. 10 hrs.

No. 10. Mixture. Quartz .25 g. cm^2 (83%). Chalcopyrite .05 g. cm^2 (17%). Lines due to chalcopyrite alone are indicated just above the print. 17 hrs.

No. 11. Mixture. Pyrite .07 g. cm^2 (54%). Pyrrhotite .06 g. cm^2 (46%). Lines due to pyrrhotite alone are indicated just above the print. 18 hrs.

No. 12. Mixture. Bornite .04 g. cm^2 (80%). Chalcopyrite .01 g. cm^2 (20%). Lines due to chalcopyrite alone are indicated just above the print. 20 hrs.

eral in question. For further guidance the positive prints of a number of patterns are presented in Plates I. and II., care being taken to make reproductions as near actual size as the processes of printing allow. These prints bring out variations in intensity that cannot be shown in the plotted patterns.

The specimens used were secured from the laboratories of Mineralogy and Economic Geology at Stanford University through the courtesy of Professors A. F. Rogers and C. F. Tolman. Several limonite specimens were kindly furnished by Dr. H. W. Morse.

Isometric Minerals.—The first isometric pattern shown is that of sodium chloride, which, as has been previously stated has been used as a standard in testing film holders.

The next is galena [27] and it is interesting to compare the pattern for galena with that for sodium chloride since the two have the same crystal structure. The pattern for galena is computed in Table III. only α-lines being measured, although both α and β-lines appear in the picture (Plate I.). The β-lines shown in the pattern will give the same spacing as the corresponding α-lines if the proper wave-length is employed. In the formula for diffraction, if .63110 Å is used for λ in the case of a β-line the spacing d will be found to be the same as that for the corresponding α-line where .70783 Å is used. When zircon filters are employed the β-lines may be largely eliminated although the exposure is lengthened. The series of ratios for galena corresponds to the spacing for the simple cube space-lattice computed in the same way as in the case of sodium chloride.

Thus galena may be seen to have the same internal structure as sodium chloride but with greater distances between corresponding planes of atoms. This relation is at once evident from an inspection of the two patterns. They contain the same number of lines in the same relative positions and show the same variations in intensity aside from that due to a difference in the length of exposure. They differ only in the distance from the

[27] The crystal structure of galena was first determined by the Braggs who used the spectrometer method.

undeviated beam. The variation in distance, however, is sufficient to make the two distinctive.

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TABLE III.

COMPUTATIONS FOR GALENA.

Experimental.			Theoretical.	
Arc in mm.	d in Å.	Ratios 2.936 = unity.	Ratios for Simple Cube.	Indices of Form.
36.4 (?)	2.96		1.000	(100)
52.0	2.09	.710	.707	(110)
63.8	1.70	.578	.577	(111)
74.0	1.47		.500	(100) $n = 2$
82.7	1.31	.447	.447	(210)
91.0	1.20	.408	.408	(211)
105.1	1.045	.355	.354	(110)
112.2	.980	.334	.333	(221) or (100) $n = 2$
118.9	.928	.316	.316	(310)
125.0	.886	.302	.301	(311)

The sphalerite samples were from Santander, Spain, containing a fraction of one per cent. of iron and from Breitenbrunn, Saxony, with a large amount of iron replacing zinc. The two gave the same patterns, which upon computation show the atoms to be arranged according to the face-centered cube lattice. Evidently the iron in the (Zn, Fe)S produces no measurable displacement of the atomic planes from that in the ZnS. If the chemical theory of atomic replacement is accepted, this is probably due to the fact that the atomic volumes of the two elements iron and zinc in this compound are so near together that the replacement of a small number of zinc atoms by iron atoms does not cause a sufficient change in the size of the structure to move the lines of the diffraction pattern.

Pyrite and cobaltite are shown together on the chart as an example of isomorphism. The cobalt and arsenic atoms of cobaltite CoAsS produce a closer spacing of the lines in the pattern than do the iron and sulphur atoms in pyrite FeS_2. From which it may be inferred that arsenic has a larger atomic volume

in such a compound than sulphur. Thus it may be seen that these two isomorphous minerals produce the same arrangment of lines but with a different spacing.

The spinel group furnishes the most striking example of the effect of isomorphism of any of the minerals studied. The magnetite and franklinite specimens gave identical patterns (Plate I.). Magnetite has the composition $FeFe_2O_4$, while in the absence of a chemical analysis it is not certain whether the franklinite formula would be $(Zn, Mn, Fe)Fe_2O_4$ or $(Fe, Zn, Mn)Fe_2O_4$ although the former is more likely. If the formula in which the zinc predominates over the ferrous iron is accepted; the explanation of the identical nature of the two patterns would seem to lie in the fact that the zinc, manganese and a small amount of ferrous iron combine to produce the same effect in franklinite as is caused by the ferrous iron alone in magnetite. This is probably the case and zinc and iron atoms in the two minerals may have the same volumes. On the other hand, if the ferrous iron should predominate it would appear that the franklinite is in reality a zinc-bearing magnetite and the same considerations may apply that have just been mentioned in the case of sphalerite. The other two minerals tested in the group, chromite $(Fe, Mg)(Cr, Al)_2O_4$ and spinel $MgAl_2O_4$, give broader spacings for diffraction lines than the magnetite or franklinite spacing, and when compared with each other the spinel spacings are broader than those for chromite.

This group is interesting from the determinative standpoint, because it indicates that in some cases of isomorphism it may not be possible to distinguish two different minerals by this method. Where the members of a group are sufficiently different in chemical composition, however, they can be determined readily.

Tetrahedrite furnishes an example of the variations that may occur in one mineral due to isomorphism. Three samples were tried; two of the samples, tetrahedrite and silver-bearing tetrahedrite, gave identical patterns, while the third, mercurial tetrahedrite, gave a similar pattern but with a slightly broader spac-

ing. This is particularly surprising because one would expect the mercury atoms to be larger and hence produce a smaller spacing of lines, but apparently the atomic distances are smaller and hence the diffraction lines are farther apart. The variations in the chemical composition of tetrahedrite, however, are so complex that the information at hand is insufficient to attempt an explanation of the changes in the lines. Nevertheless, it is important to note that the three patterns are distinct from those of other minerals and are nearly identical with each other.

Bornite shows a pattern which is unique in that one heavy line stands out with an intensity greater than any of the rest. When bornite is present in mixtures of minerals this strong line forms a very convenient means of recognition.

Orthorhombic Minerals.—Stibnite and bismuthinite furnish examples of isomorphism similar to those encountered in the isometric group. The patterns are similar but the distances differ, the lines for bismuthinite being more closely spaced.

A sample of goethite, the ferric oxide monohydrate, was tested and the pattern compared with the patterns for a number of samples of the apparently amorphous limonite. These limonites varied from fine ultramicroscopic powders to one sample that was isotropic. The patterns of all, however, were alike and identical with goethite. The supposedly amorphous material produces even better lines than those observed for goethite in some cases. It seems at least possible from this X-ray data that amorphous limonite does not exist and that "limonite" is merely a mode of aggregation for the orthorhombic mineral goethite. This confirms the chemical study of Posnjak, Allen and Merwin of the Geophysical Laboratory[28] which throws doubt upon the classification of limonite as a distinct mineral. In view of the results of X-ray work in this case the possibility of the application of this type of study to ultramicroscopic aggregates appears important.

The orthorhombic mineral marcasite FeS_2 is shown to give a pattern distinct from pyrite the isometric FeS_2, which brings out

[28] Posnjak, Allen, and Merwin, *Am. Jour. Sci.*, 47, p. 311, May, 1919.

the point that dimorphous minerals should be easily recognized by this method, and illustrates the fact that the atomic arrangment is just as important a factor in determining the pattern as the chemical composition.

The pattern for chalcocite Cu_2S is different from that of covellite CuS, although the photographs of chalcocite secured gave very few lines in spite of repeated trials with varying technique.

The orthorhombic minerals, arsenopyrite, pyrrhotite, and enargite have distinct diffraction patterns. Arsenopyrite may be easily distinguished from marcasite and it is surprising that a greater similarity does not exist between the patterns for the two minerals since the minerals themselves are isomorphous. In this connection, however, it is interesting to note that there is a considerable divergence in the axial ratios of the two which must indicate a corresponding variation in the shape of space-lattice and probably accounts for the difference between the patterns.

Tetragonal Minerals.—The two tetragonal minerals included in the chart are chalcopyrite and cassiterite.

The samples of cassiterite are from two localities; the first, transparent Bolivian cassiterite and the second, wood tin from Cornwall. The two produce identical patterns which establishes the fact that "wood tin" is merely a variety of cassiterite. The "wood tin" is more finely crystalline and produces smoother lines than those that are given by the other sample.

Hexagonal Minerals.—The hexagonal minerals ilmenite $FeTiO_3$ and hematite Fe_2O_3 furnish another example of isomorphism that follows the same rule which governs the cases already discussed. Covellite gives a distinct pattern which allows it to be easily distinguished from the other sulphides of copper.

Calcite and quartz are included because of their importance as gangue minerals. It is interesting to note, however, that the pattern for chalcedony is identical with that for quartz. This agrees with the work of Washburn and Navias[29] and indicates that chalcedony, although considered by many as a distinct mineral, is probably a microcrystalline form of quartz.

[29] Washburn, E. W., and Navias, L., *J. Am. Ceram. Soc.*, 5, 565–585, 1922.

Amorphous Minerals.—As previously stated amorphous minerals are supposed to have no crystal structure and consequently should not produce diffraction lines. A few supposedly amorphous minerals were tested but opal is the only one found that gives no lines. This is a distinct advantage in the application of the method to determinative work, for the smaller the number of amorphous minerals the more generally applicable the method.

Aggregations.—The mode of aggregation apparently has no effect upon the spacing or intensity of the lines in a diffraction pattern. In order to illustrate this point two varieties of hematite (specular hematite and pencil ore) were tried. The patterns given were the same in each case, except for the fact that the pencil ore was in a more finely crystalline condition and consequently produced sharper lines. The diffraction photographs of "wood tin" and cassiterite already mentioned as being identical, and those for chalcedony and quartz furnish further confirmation of this point. In each case the fine crystalline material gives the best diffraction lines.

Mineral Mixtures.—The diffraction patterns of three representative mineral mixtures are shown in Plate II. A series of such mixtures has been photographed but lack of space prevents the reproduction of more at the present time. A preliminary study of the diffraction photographs of mixtures indicates that under favorable conditions of technique the diffraction pattern for a mineral mixture contains the patterns of the components superimposed upon each other.

To illustrate, consider the diffraction pattern for the chalcopyrite-quartz mixture. It is the same that would be produced by superimposing a pattern for chalcopyrite upon one for quartz. A few of the lines coincide, while the remainder are distinctly either due to one or the other of the two minerals independently. The same has been found to be the case in all of the mixtures tried. Lines that coincide exactly are stronger in the mixture than in the individual patterns, while non-coincident lines appear in about the same intensity.

Large variations in the intensity of the lines in the pattern for

a mixture may be introduced by varying the weights of the component minerals in the sample. When the various minerals are present in about optimum weights (see the discussion of technique) the lines due to each will have their maximum development. In the pyrite-pyrrhotite mixture as well as in the quartz-chalcopyrite mixture already referred to the mineral components were present in about optimum amounts, and the lines due to each mineral in the mixture compare favorably in intensity with the lines due to the same mineral photographed independently. On the other hand, if this optimum is greatly exceeded or if there is not enough of the sample present the lines will decrease in intensity, either due to absorption in case the sample is too thick, or because of a lack of scattering power if there is not a sufficient amount of the mineral present. It is not certain just how far the weights of the minerals could be varied in all cases and still produce lines. In the case of bornite-chalcopyrite mixtures several variations have been tried. One sample containing bornite in an optimum amount and 93 per cent. of the mixture together with 7 per cent. of chalcopyrite showed faint but measurable lines due to chalcopyrite in the midst of a much stronger bornite pattern. The print at the bottom of Plate II. shows about the same effect but the per cent. of chalcopyrite in the sample was higher. It seems probable from preliminary work that at least 7 per cent. of one ore-mineral may be distinguished in the presence of another and it is not unlikely that under favorable conditions of exposure the percentage would be much lower. In order to produce good lines, however, the mineral must be present in about an optimum amount. This is a disadvantage from the determinative standpoint.

The number of minerals that can be determined in the persence of each other is limited by the number of lines that are produced in the pattern. If more than two or three minerals are present in a mixture, difficulties are apt to arise due to a multiplicity of lines.

It is altogether likely that ore-minerals may be easily determined in the presence of light gangue-minerals by this method.

A galena-calcite mixture was tested in which calcite made up 80 per cent. of the sample by weight and yet was far enough below the optimum for calcite to prevent calcite lines from appearing in the diffraction photograph. Although galena made up only 20 per cent. of the sample it was present in an optimum amount and produced a good pattern.

CONCLUSIONS.

The diffraction patterns of a number of opaque ore-minerals have been photographed with the expectation that they may serve as standards for future work. In general, these patterns are distinctive for different minerals and depend upon both the chemical composition and atomic arrangment of the mineral in question. In the case of franklinite and magnetite, however, identical patterns were secured, which indicates that difficulties may be encountered in distinguishing isomorphous minerals. Dimorphous minerals, on the other hand should be distinguished without much trouble.

The technique has a considerable influence upon the clearness of the lines in a diffraction pattern. In order to secure good lines, the mineral in the sample should be present in approximately an optimum weight. It seems probable, however, that in favorable cases about 10 per cent., or even less, of one ore-mineral may be distinguished in the presence of another.

Under favorable conditions of exposure the diffraction pattern for a mixture of minerals contains the diffraction patterns for the individual components superimposed upon each other. Two minerals may be distinguished in the presence of each other, but it is advisable to limit the number of minerals in a mixture to two or three in order to avoid a diffraction pattern with a multiplicity of lines. It is likely that mixtures of isomorphous minerals in the same group would, in some cases at least, cause considerable difficulty in determination.

The presence of a considerable amount of light gangue-mineral should not interfere in distinguishing heavy ore-minerals.

The chief disadvantage which the powder method offers in its

application to mineral determination is the fact that costly apparatus is generally required, but this has been offset to a large degree by the construction of the less expensive outfit already described. With either, however, the exposures are bound to be long and the apparatus can hardly be operated to advantage unless a large number of samples are to be tested at once.

In conclusion the fact must be emphasized that this work cannot be considered as more than an introduction to what promises to be an important field of mineralogical research. However, the scientific application of the method to such problems as have been presented in the cases of "limonite" and goethite, chalcedony and quartz, as well as "wood tin" and cassiterite seems to be of considerable importance. In fact, the powder method appears at present to be more promising from the standpoint of determining scientific fundamentals that are beyond the limits of the microscope than from the standpoint of determination alone.

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SOME EXPERIMENTS ON CAPILLARITY AND OIL MIGRATION.

WILLIAM L. RUSSELL.

THE different theories of oil accumulation are interesting not alone to science; they are of great practical importance in the discovery of oil pools. If the oil has accumulated in anticlines by migrating up the dip due to its buoyancy, the size of the resultant oil pool should increase with the area of drainage down the dip. If the oil was carried to the domes by hydraulic currents, the strength of the currents and the area of drainage in the direction from which the currents came are of prime importance. Similarly, if the migration of the oil and the location of the pool are determined by capillary forces, a different set of factors must be considered in locating a test.

SUMMARY OF PRECEDING LITERATURE.

In recent literature there has been much discussion relative to these theories. That capillary forces have been important in moving the oil has been supported by many geologists, notably by Washburne and McCoy. Washburne long ago stated [1] that because crude oils have about one third the surface tension of water, water will drive the oil out of very fine sediments with considerable pressure. He believes, however, that the high pressures in oil sands can not be due to capillarity. He also suggests that the globules of oil are forced from the shales by capillarity. McCoy [2] described some experiments in which oil was driven out of muds by capillarity, and concentrated in the coarsest sands, in one case by moving downwards.[3, 4] In one experiment he found that a current of water failed to move a small volume of oil from a mass of 10-mesh sand grains into the surrounding 20-

[1] For references see bibliography at end of article.

mesh sand grains. The velocities or heads used in this experiment were not given, but they were probably much greater than those which would occur naturally in oil sands. In 1916 he says:[5]

> This paper does not attempt to say that capillary forces have ever caused anticlines in nature, but merely points out that possibility. At least one thing is borne out by the above experiments: that the segregation of oil and water in openings of the ordinary oil rocks is not according to the general hydrostatic idea, but that the water forces the oil into the larger openings regardless of structure. This does not do away with the general anticlinal theory of accumulation. On the contrary, it substantiates this theory, as the larger openings are more often on the crest of the anticline regardless as to whether the oil caused the fold or whether the oil migrated there after the fold had been made.

In 1919 he writes:[6]

> The pressure on the oil as it exists in the porous strata is the same as that on the water which previously occupied the space. A volume of water replaces approximately an equal volume of oil. Therefore, the pressure on the reservoir remains the same. When the relation of oil to advancing water is such that the oil may be trapped and forced forward by capillary water, considerable pressure may accumulate on the oil due entirely to the capillary action of the water. Such conditions would be local if ever present and of little importance in commercial oil pools.

McCoy also points out the importance of joints in permitting the migration of oil from the shale into the sandstone. Recently Cook[7] has described an experiment in which oil was driven by the capillary force of water out of a fine sand and out a capillary tube. The only outlet of the tube containing the fine sand was the capillary tube. The oil ran out through the central portion of the capillary tube and the water ran in between the oil and the walls of the glass tube. Cook also states that the capillary force can not be calculated by the usual methods, because of the cohesion of the liquids involved.

Mills[8] has also described some interesting experiments relative to the migration of oil by buoyancy and hydraulic currents. He concludes that oil is accumulated by buoyancy and hydraulic

currents. Munn[9] and Rich[10] both have advocated the theory that oil pools are due to the movement of oil globules by hydraulic currents. Rich describes an experiment in which sand with diameters of ¼ to ½ mm. was placed in a vertical tube, and a current was allowed to run through it at a rate of about a drop per second. This current carried globules of oil along with it, but the velocity was enormously greater than that of natural hydraulic currents in oil sandstones.

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Others have considered that moving gas bubbles have been important in oil accumulation. The oil tends to form a film around the gas bubble, as has been known for many years. Thiel[11] describes an interesting experiment in which a glass tube 1 inch in diameter and 4 feet long was bent into the form of an anticline, filled with crushed quartzite which had been passed through a 20-mesh screen and impregnated with crude oil, and filled with sea water which had been acidified with acetic acid to ½ of one per cent. A few inches of powdered magnesian limestone were added at the ends and the tube was corked. The action of the acetic acid on the limestone generated carbon dioxide under considerable pressure, and it was found that the oil and gas migrated to the top of the anticline, with the gas above the oil. As Thiel says, the oil could not have been carried by the gas bubbles, for in some cases the oil migrated in the opposite direction from the movement of the gas. In this case it is possible that the gas lessened the surface tension, adhesion, or viscosity of the liquids.

Dodd[12] describes an experiment in which a glass tube ⅞-inch in diameter and 30 inches long was filled with an oil impregnated sand and a water sand. Under a pressure of 70 inches head of water (hydraulic gradient ⅞) the globules of oil from the oil sand were driven into the water sand, where many of them were trapped in the pores. It was found that minute bubbles of gas carried in a water current were more effective in carrying the oil than a current of water alone. Recently Mills[13] has put forth the theory that the sudden escape of gas through open faults has caused the accumulation of oil in certain cases.

The theory of the hydraulic action of currents in causing oil

accumulation by carrying globules of oil or bubbles of gas rests on a very insecure experimental basis, for the experiments have not been carried on with the same velocities of hydraulic gradients that would occur naturally. Also the manner in which oil and gas is moved through a water sand has not been given due consideration.

In the present paper evidence will be put forth to show that oil was driven from the shales or limestones, in which it originated, into the sandstones in masses large enough to be affected by buoyancy. These masses then threaded their way towards the tops of the anticlines by differences of head between the oil and water due to the lower specific gravity of the oil.

It is not difficult to cause the formation of miniature oil pools by artificial means. While these may have a superficial resemblance to natural oil pools, it is impossible to duplicate in the laboratory all the conditions of the field. Hence it is necessary to know the laws governing oil accumulation in order to ascertain whether these laboratory oil pools could be formed in nature by the same processes. In view of these facts it seemed advisable to try and discover the laws of oil accumulation first of all, instead of creating artificial oil pools.

It should be borne in mind that the experiments described below were preliminary experiments, performed with extremely simple and inexpensive apparatus.

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THE PURPOSE OF THE EXPERIMENTS.

The experiments described below were undertaken primarily for the New York State Geological Survey, in order to gather information relative to the commercial extraction of oil from oil sands. The data bearing on the extraction of oil will be dis-

cussed in a Bulletin of the New York State Museum; in this paper only the experiments relative to the accumulation and migration of oil will be considered. The latter were carried on to ascertain if there was any capillary force causing water to drive oil out of fine sands; to measure the relative intensities of this force and the diameters of the sand grains in which it takes place; to determine the minimum sizes of oil masses necessary to cause them to migrate upward through water sands by virtue of their buoyancy; and to determine if the velocities of hydraulic currents which could occur in oil sands would be able to move through them globules of oil, or bubbles of gas coated with oil.

DESCRIPTION OF APPARATUS.

The apparatus for measuring capillary force consisted of a large glass tube, having a length of 8 or 12 inches and a bore 0.9 inch in diameter, into one end of which was cemented a fine glass tube, having a bore 0.2 inch in diameter. The fine glass tube was bent at right angles near the large glass tube, and extended up vertically for a suitable distance. The intensity of the capillary force tending to cause water to drive oil out of fine sands was measured as follows: A sand saturated with oil was placed in the portion of the large tube nearest the fine tube. The remainder of the large tube was filled with water, and more of the same sand was poured in, rammed down, and held against the oil sand by a wad of cheese cloth. The large tube was then immersed in water in a pan. When there was a capillary force between the oil-water surface, the oil was displaced from out of the oil sand and driven up the fine tube. The amount of rise of the oil in the fine tube above the water level in the pan, minus a small correction due to the buoyancy of the oil below the water level, gave a measure of the capillary force.

The force necessary to drive oil into water sands, and water into oil sands is, as will be shown later, important in determining whether an oil mass of a given size will migrate due to buoyancy. In measuring the force necessary to drive water into oil sands, it was found that the force necessary to cause the water to enter

the oil sand is greater than the force necessary to impel the water through the sand after once entering it. In Table I. the force necessary to drive oil or water into a sand saturated with the other liquid is called initial head, the force necessary to cause it to continue to migrate through it after it had once entered it is called migrating head. The initial head for water was measured in the following manner: A glass tube, the bore 0.9 inch in diameter, was placed in a beaker of oil so that there was only a very thin crack between the lower edge of the tube and the bottom of the beaker. Sand was then poured into the oil in the bottom of the tube, until the level of this oil-saturated sand rose to the level of the oil in the beaker. Water was then poured into the tube very gradually until there was just sufficient pressure to cause the water to enter the oil sand. The height of the water column was then the initial head for water. The crack between the bottom of the tube and the bottom of the beaker afforded an exit for the displaced oil, but was too fine to allow the sand to pass through.

The migrating heads for oil were measured as follows: The arrangement of the tubes was the same as in the capillarity measurements. The large glass tube was filled with the water saturated sand, immersed in water in a pan, and oil was poured into the fine tube until the oil began to migrate into the water sand. As the oil entered the water sand, the head of oil in the fine tube grew less and less until finally the movement stopped. Then the height of the oil in the fine tube above the level of the water in the pan was a measure of the migrating head. The migrating heads for water were measured similarly, by reversing the relations of the liquids. It was found that, while in fairly coarse sands a slight force is necessary to keep water migrating through an oil sand, as the sands become quite fine this force grows less, and finally in very fine sands becomes negative. That is, the water is drawn into the sands. This is due to the capillary action of an oil-water surface, and is shown in Table I. as negative migrating head.

TABLE I.

RESULTS OF EXPERIMENTS ON THE CAPILLARY FORCES OF AN OIL-WATER SURFACE, AND THE HEADS NECESSARY TO CAUSE OIL TO MIGRATE INTO A WATER SAND, AND WATER TO MIGRATE INTO AN OIL SAND, WITH SANDS OF VARIOUS DIAMETERS.

Sand, Diameter of Grains in Mm.	Oil into Water				Water into Oil	
	Initial.		Migrating		Initial	Migrating
	In. Head of Oil	In. Head of Water	In. Head of Oil	In. Head of Water	In. Head.	In. Head.
0.833 to 1.168	0.3	0.3	0.3	0.3	0.3	0.2
0.589 to 0.833	0.8	0.7	0.8	0.7	0.5	0.2
0.417 to 0.589	1.0	0.8	0.9	0.8	0.8	0.2
0.295 to 0.417	1.25	1.0	1.2	1.0	1.2	0.1
.208 to .295	1.5	1.2	1.3	1.1	1.9	0.0
.147 to .208			2.5	2.0	2.5	− 0.27
.104 to .147						− 0.5
.074 to .104						− 1.1
Less than .051						− 6.6 +
Fine quartz powder sifted through silk						−14.1 +
.147 to .208, 28% .147 to .104	3.6	3.0				− 0.9
.147 to .104, 6% less than .104	6.7	5.6	3.6	3.0	4.3	− 0.6

The apparatus just described has the advantage of being very simple and easy to construct. Owing to the difficulty of securing the same degree of compaction and porosity inside the tubes, this apparatus is capable of indicating only the relative magnitudes of the forces involved, and not their exact amounts.

The apparatus used in other experiments can best be described along with the results of the experiments.

RESULTS OF EXPERIMENTS ON CAPILLARITY.

1. *The Nature of the Capillary Forces.*

A study of the previous literature concerning the effect of capillarity on oil accumulation is apt to leave one in doubt, not only as to the nature of the capillary forces, but whether there is any capillary action between an oil-water surface. The fact that the surface tension of a water-air surface is about three times that

of an oil-air surface has been cited as proof that there is a capillary force tending to draw water into a fine oil-saturated sand. Whether or not this force has any relation to the capillary forces under discussion may be doubted; certainly the surface tension of water acting alone can not draw into a sand or capillary tube. Adhesion is another fundamental property, as some writers have noted. If the liquid adheres to the walls of the capillaries, the tendency of capillarity will be to draw the liquid into them; if on the other hand it does not adhere to the walls of the capillaries, capillarity will tend to drive it out. It is, therefore, important to determine whether or not water and oil will adhere to the substances with which they are likely to come in contact.

Dodd in his experiments found that the first liquid to wet the surfaces of the sand grains continued to adhere to them, and some of the experiments of Mills suggest this also. If this is the case, the only rôle of capillarity will be to oppose all motion, and it would be impossible for water to drive oil out of shales or other rocks. Apparently, the capillarity of an oil-water surface can not be explained by surface tension and adhesion alone.

In order that capillary movement may take place, one of the liquids must be drawn over the surface of the solid in which the pores occur. That is, the molecules of the solid which are not covered by the liquid attract molecules of the liquid from their previous position, and the result is that the liquid moves over the surfaces of the pores. Once the surfaces of the pores are wet with the liquid, surface tension will cause capillarity to act. This force tending to draw a liquid over the surface of a solid will be called attractive adhesion, in order to distinguish it from ordinary or static adhesion. If the attractive adhesion draws a liquid over the surfaces of a solid that had previously been wet with a liquid of higher surface tension, capillarity will cause the liquid of lower surface tension to drive the liquid of higher surface tension out of the pores or sands which it originally saturated.

In order to throw some light on these problems, some preliminary experiments were performed. A plate of muscovite about 2 inches square was placed gently on a water surface.

The water was not drawn over the surface of the muscovite, and the plate remained floating. If a portion of the upper surface of the muscovite was covered with water by pushing it beneath the surface, the water was gradually withdrawn, except for a few scattered drops. Then some oil was poured over the water. At first the muscovite remained floating on the oil, but gradually the oil was drawn over its surface by attractive adhesion, until it was covered by the oil and sank until it reached the oil-water surface, where it remained floating indefinitely. Water and oil on smooth glass surfaces will behave in much the same manner. The oil will gradually spread over the surface, while films of water will be drawn together into drops. These experiments suggest that the attractive adhesion of oil for glass and mica is greater than that of water. There is, however, another factor that must be considered. When a liquid forms a thin film over the surface of a smooth solid, attractive adhesion and surface tension tend to oppose each other, because attractive adhesion tends to increase the area of the film, while surface tension tends to cause the film to contract and gather in drops. The force of surface tension of water is much greater than that of oil, hence the tendency for a film of water to spread out is resisted by a much greater force than is the case with a film of oil.

On the other hand, when a liquid is in a tube or a long narrow pore, the forces of attractive adhesion and surface tension do not act in direct opposition to each other. The force of attractive adhesion will tend to draw the liquid along the sides of the tube, but if the force of surface tension draws the whole surface an equal distance along the tube, the area of the surface will not be increased, provided that the tube is of a constant diameter. The same line of reasoning applies to a fine crack. Hence, in order to measure the relative intensities of the forces of attractive adhesion of oil and water, it is necessary to place them both in a fine pore or crack.

The forces of attraction can not act unless the liquid is in contact with the solid, or very close to it. Even though some oil-saturated sand or sandstone may be in contact with water,

its surface will be covered by a film of oil held there by adhesion. This should hold the water at a distance from the walls of the pores and prevent the water from being drawn into them by attractive adhesion, even though this force may act with greater intensity between the water and the sides of the pores than it does between the oil and the sides of the pores. The force of attractive adhesion can not act unless the water is driven into the pores. In order to do so it is necessary to bend the oil-water surface until it projects into the pores. This action would be resisted by surface tension; consequently it is necessary to apply a certain force to start capillary action going.

A few simple experiments were performed to illustrate the mode of action of these forces. A piece of muscovite about 3 inches square was split along the planes of cleavage, and the crack thus formed was held open by a few sand grains. The crack was then wide near the sand grains, but tapered gradually, and became extremely thin near the opposite side of the square. When oil was inserted in the crack it was of course drawn into the fine part of the crack by capillarity. If now some water were driven a little way into the fine portion of the crack, it was drawn in by the forces of attractive adhesion and surface tension, and speedily drove the oil out.

A small glass tube was then heated in a Bunsen burner and drawn out until the bore was very fine. The fine end was broken and immersed in oil, which was drawn into it by capillarity. When the fine end of the oil-filled tube was placed a short distance beneath the surface of some water, the water did not enter the tube. But when the water was driven a very short distance into the finer end of the tube, it was drawn up to the tube, driving the oil ahead of it. The oil-water surface remained stationary when it reached the coarser portion of the tube. It was then convex towards the oil, indicating that the water adhered to the walls of the tube. These simple experiments show that in fine tubes or pores water is drawn over the walls of the tubes, displacing the oil which was originally in contact with them. The surface tension of the oil-water surface then causes it to be drawn after the water as it moves along the walls.

Before any idea can be obtained of the action of capillarity in causing the migration or accumulation of oil or gas, it is necessary to know whether or not the liquids concerned will adhere to the solids in which they are contained, and which liquid has the greatest force of attractive adhesion. It has generally been assumed that water will adhere to all the substances in which oil is likely to be contained. If water does not adhere to these substances, and is not drawn up into them by attractive adhesion, capillarity as generally understood can not play a part in oil migration or accumulation. A few tests were therefore made to ascertain what substances oil and water adhere to. It was found that oil will adhere to quartz, glass, clay, mica, quartz grains coated with natural paraffin, and powdered soapstone, and will be drawn up into fine particles of these substances when they are dry. Water will adhere to particles of quartz, clay, mica, and oil shale, and will be drawn into them when they are dry. It was not possible to make water adhere to fragments of an oil sandstone, even when this had been heated to redness and allowed to cool. It was also impossible to make water adhere to commercial powdered soapstone.

The results of experiments on the capillary forces are shown in Table I. The initial head necessary to drive oil into a water sand, and the migrating head, are the same within the limits of the experimental error. This is what is to be expected, according to the theory of capillary action already developed, for, as the oil is not affected by attractive adhesion when the walls of the pores are coated with water, the force necessary to drive the oil through the pores of the sand should be the same as the force necessary to cause it to enter the sand. In the case of water entering an oil sand, on the other hand, the force of attractive adhesion begins to act when the pores are so small that attractive adhesion and surface tension no longer act in direct opposition to each other. This causes the migrating head to be much less than the initial head for the fine sands. Unfortunately, different methods of compacting the sands and keeping them pressed together give different results. When oil is driven into a very fine water

sand there is a tendency, unless the sand is tightly compacted, for the oil to wedge the sand apart and form numerous cracks filled with oil. When water is drawn by capillarity into a very fine loose oil sand there is also a tendency for a crack to form between the oil sand and the water sand. The pull of the capillary force on the sand grains causes them to be drawn towards the advancing water. This crack often effectively stops the capillary migration.

In the case of the sand less than 0.051 mm. in diameter, and the fine quartz powder sifted through silk, migration stopped because the oil had nearly all been driven up out of the large tube into the fine tube. As the migration might have gone further if there had been more oil in the large tube, the values are marked plus.

An attempt was also made to observe the effect of capillarity in oil-soaked clay. The clay was dried by heating, a portion was soaked in oil, and the oil-soaked portion was placed in the lower closed end of a test tube. Water-soaked clay was held against the oil-soaked portion by a wad of cloth, which in turn was pressed down by screwing a perforated iron cap over the mouth of the test tube. The test tube was then inverted and stood in a pan of water. The oil was driven down out of the oil-soaked clay by capillarity, and filled cracks which were opened up in the clay by the capillary force.

The results tabulated in Table I. indicate that in loose sands capillarity causes water to be drawn into an oil sand with a slight force when the diameter of the grains is less than 0.147 to 0.208 mm. The capillary forces are doubtless considerably affected by the degree of sorting of the sand grains and by the compaction and amount of cementation. Capillary phenomena which occur in loose, well-sorted sands composed of grains of a certain degree of fineness, might occur in much coarser sands or sandstones composed of poorly sorted, well compacted, or highly cemented grains. The term "effective diameter" of the sand grains will be used to indicate that the set of capillary forces is the same as would occur in loose, well-sorted sands of the given

diameter. Thus a firmly cemented sandstone, the grains of which averaged 1.0 mm. in diameter, might have an effective diameter of only 0.1 mm., owing to the reduction in the sizes of the pores.

Table I. points to the following conclusions regarding the action of the capillary forces in oil migration and accumulation. (1) In sands having an effective diameter greater than about 0.25 mm. there is no capillary force between an oil-water surface, tending to drive the oil into the larger pores. (2) Where the effective diameter of the sand grains is greater than 0.074 mm., this capillary force is very small, only equal to one or two inches head of water. (3) As the effective diameter of the grains becomes still smaller, approaching that of clays, the capillary force doubtless becomes very much larger. (4) In sands having an effective diameter over 0.074 mm., capillary forces are not capable of causing a difference of more than a few feet in the elevations of the oil-water surface. In other words, capillarity can only drive oil a few feet downward through a water sand against the force of the buoyancy of the oil. This point will be considered below in greater detail.

If these conclusions are correct, capillary forces are not important in influencing the migration of oil once it has reached the sandstones, except possibly in extremely fine or highly cemented sandstones. The migration of oil from its source in shales or limestones may be due to capillarity, provided that no substances to which water will not adhere are deposited on the surfaces of the pores of the source rocks. The compaction of the sediments, tectonic pressures, and gas pressure are other possible causes of this migration.

It is customary to calculate the force of capillarity in sands upon the basis of the surface tension. However, as the surface tension only becomes operative after attractive adhesion has displaced the oil from the walls of the pores, and covered them with water, it is evident that the capillary force can be no greater than the force of attractive adhesion, no matter how great the surface tension may be. If the force of attractive adhesion is

greater than surface tension, then the capillary force may be calculated upon the basis of surface tension. If on the other hand the force of attractive adhesion is less than the surface tension, the capillary force can not be greater than the force of attractive adhesion, and calculations made in the usual method would give excessively large results.

The force necessary to drive oil into a water sand is important because of its influence on the operation of the capillary forces, and because it indicates the size a mass of oil would have to reach before it could rise through a water-sand by virtue of its buoyancy. In all the sands tested, this force was found to be greater than the capillary force. If this relation is generally true, as seems likely, it indicates that, if a solid mass of oil-soaked materials, whether fine or coarse, were completely surrounded by water-saturated materials of the same effective diameters, the oil could not be driven out by capillarity. No matter how great the capillary force was, the force required to move the oil through the oil-saturated materials would be greater. This means that oil could only be driven out of an oil shale through a fault, crevice, joint, or coarse lens.

The pressure that may be developed by capillary forces alone depends on the character of the materials cut by the oil-water surface in the sand or porous reservoir. If we assume that the water displaced from the sands is able to run into the shales and limestones and replace the oil that is driven out of them, then the maximum pressure which can be developed by purely capillary forces is equal to the force necessary to drive oil into the coarsest pores cut by oil-water surface, or gas-water surface. If the pressure were any larger than that, the oil would simply run into the coarsest pores until the pressure was relieved. This means that the pressure due to capillarity is negligible provided that only part of the reservoir is filled with oil and gas. When the whole of the sand lens is filled with oil and gas, then the pressure which capillarity could develop would be measured by the force necessary to drive the oil and gas into the shales or limestones surrounding. As this latter force is probably very large, it is evi-

dent that capillarity might accumulate great pressures under such circumstances.

Experiments Relative to the Rise of Oil Due to Buoyancy.

The column of Table I. showing the force necessary to drive oil into water sands is important in studying the migration of oil due to its buoyancy. The first step to a consideration of this problem is to arrive at a conception of the laws governing the rise of oil through water sands. The consideration of some simple cases may be of assistance in illustrating the action of these laws. Let us assume that a tube filled with oil-saturated sand is placed vertically in a water-saturated sand. As the oil in the tube is lighter than the water in the sand surrounding it, the pressure of the column of oil in the oil sand is less than the pressure of a column of water of the same dimensions in the water sand. The difference in the pressures at the bases of the two columns is equal to the height of the oil column multiplied by the difference in the densities of the oil and the water. The density of waters associated with oil is generally greater than 1.0, owing to their salty content. If, for example, the hydrostatic pressure exerted by a column of water one foot high were 0.5 lbs. per square inch, and the pressure exerted by a column of oil of the same height is 0.4 lbs. per square inch, then in the case under consideration the difference in pressure would be 1 lb. per square inch for every 10 feet of height of the tube. The liquids at the base of the tube are under the hydrostatic pressure of the water column, which is transmitted in all directions. If the hydrostatic pressure of the water on the oil at the base of the tube were equal to the pressure of the column above the base of the tube, there would be no tendency to motion. As, however, the hydrostatic pressure of the water column is greater than the hydrostatic pressure of the column of liquids above the base of the tube, there is an unbalanced force tending to drive the oil up the tube, which, in the base assumed, would equal to 1 lb. per square inch for every 10 feet of height of the tube. Hence, if the force resisting this force were less than 1 lb. per square inch

and the tube were 10 feet or more in height, motion would take place.

It should be clearly understood that only the differences in the elevations of the bottom and top of the tube are concerned in this reaction. If the differences of elevation between the top and bottom of two tubes are alike, the differences in hydrostatic pressures of the oil and water columns will be the same, no matter what the angle of inclination of the tubes is. Therefore, forces tending to cause motion are the same, though of course when motion does occur it will take place at a much slower rate in the case of the inclined tube, owing to its greater length.

Let us now consider a body of oil in a water sand. If the difference of elevation between the highest and lowest parts of the oil body is but slightly greater than that necessary to cause the oil to rise by buoyancy, then the oil in the highest parts of the mass would rise, displacing the overlying water. In the same manner, the oil in the lowest part of the mass would rise and its place would be taken by water. The boundary between the oil and water in the middle portions of the oil mass would remain stationary, because there would not be enough difference of elevation to cause it to move. In other words, the effect would be much the same as though the oil were in a pipe open at the base and top, and the case is similar to that of the column of oil just considered.

Let D = the specific gravity of the oil
d = the specific gravity of the water
H = the difference in elevation between the highest and lowest portions of the same continuous oil mass
F = the force necessary to drive oil into water-saturated sands of the same effective diameter as that in which the oil body is immersed, and
f = the force necessary to drive water into an oil sand of the same effective diameter as the sand under consideration,

then the oil will rise owing to its buoyancy when $(d - D) \times H$ is greater than $F + f$. f is so small that it may be neglected.

The force F is that shown under the initial or migrating heads

of oil in Table I. As previously stated, these forces are probably the same, or nearly the same, for oil. The differences in the experimental measurements of these two forces are probably due to the tendency of the oil to enter the very fine sands by forcing the grains aside. According to Table I., the force F for sands having an effective diameter of 0.147 to 0.208 mm. is 2.0 inches head of water. Hence, if an oil body having a specific gravity of 0.85 were immersed in such a sand in brine having a density of 1.05, the vertical length necessary to cause the oil to rise by buoyancy would be

$$(1.05 - 0.85)\ H = 2.0,$$
$$\text{or} \qquad H = 10 \text{ inches.}$$

Hence, if the oil body measured 10 inches from top to bottom, the oil would rise. If an accumulation of oil occurred in this sand, the maximum differences of level that could exist permanently in the lower surface of the oil, where it touched the salt water, would be 10 inches.

Salt water has a somewhat greater capillary force than fresh water. This would tend to increase somewhat the differences of elevation necessary to cause motion. Surface tension is greatly lowered by increases of temperature, and perhaps also by dissolved gases. These factors may lower the figures considerably.

If a water sand into which oil was migrating should consist of several layers of varying degrees of fineness, the oil would of course enter the coarsest, but the difference in the elevation of the oil-water surface thus produced could not be permanently greater than the differences of elevation necessary to cause oil to migrate by buoyancy into the finest of the layers.

The conclusions resulting from the investigation of the migration of oil by buoyancy are as follows: Except in the case of oil sands having effective diameter less than 0.074 mm., bodies of oil extending more than a few feet vertically would migrate by virtue of their buoyancy, and differences in the elevation of the oil water surface due to surface tension or capillarity could not exceed a few feet.

It should be understood that the important factor is the difference in elevation and not the angle of dip. Misunderstandings on this point have led to misinterpretation of experimental data. Some experimentors have sought to test the ability of oil to migrate up dips of various angles by placing the oil sand and the water sand in a glass tube and inclining the tube at various angles. In these experiments the surface separating the oil and water was generally at right angles to the length of the tube. In other words, the oil-water surface was practically flat when the tube was vertical. Therefore it is evident that the force tending to cause the oil to migrate owing to its buoyancy was actually much greater when the tube was horizontal than when it was vertical. If the tube were 1 inch in diameter, and horizontal, the difference in elevation of the oil-water surface would be 1 inch. If the tube were vertical, it would be nearly zero.

As already stated, it is likely that the oil reaches the oil sand through joints, fissures, or other channels. If this is the case the oil must have issued into the oil sands in small subterranean oil seeps. If the oil which first came through the seeps remained stationary, a mass of oil large enough to rise by buoyancy would finally accumulate. Hence, the migration of oil may be explained without the action of capillarity or hydraulic currents.

In order to test these conclusions, the following experiment

TABLE II.

SCREEN ANALYSIS OF OLEAN SANDSTONE, OF POTTSVILLE PENNSYLVANIAN AGE, FROM THE OLEAN CONGLOMERATE AT ROCK CITY, N. Y.

Diameter of Grains in Mm.	Weight in Grams	Per Cent
0.833– 1.68	.....	1
0.589–0.833	1.845	10
0.417–0.589	9.050	47
0.295–0.417	5.570	29
0.208–0.295	1.650	9
0.147–0.208	0.550	3
0.104–0.147	0.220	1
0.074–0.104	0.085	0.4
through 0.074	trace	

was performed. A piece of the Olean Conglomerate from Rock

City, N. Y., the screen analysis of which is shown in Table II., was cemented into a pipe, and saturated with water. It was found that oil would flow through this rock under a pressure of about 4 inches head of water. If the difference in the specific gravity of the oil and water were 0.25, then it is evident that masses of oil extending more than 16 inches vertically would rise in such a sand by buoyancy, provided that the salinity of the water, temperature, and dissolved gases did not affect the result.

CONCLUSIONS AS TO HYDRAULIC CURRENTS.

We are now in a position to consider the possibility of hydraulic currents occurring in oil sands, and their effect on oil migration and accumulation, if they did occur. There is of course no doubt that globules or masses of oil or gas can be moved by hydraulic currents. The question is whether hydraulic currents that are capable of moving these globules have occurred in oil sands. The hydraulic currents used in most experiments on the migration of petroleum are very much faster than could be expected to occur in oil sands. The hydraulic gradients used are usually 0.5, 1, or more, which is enormously greater than those likely to be found in oil sands. The hydraulic gradient is obtained by dividing the head of water causing the current by the distance the current traverses. If a globule of oil is to be driven through a water sand, differences of pressure on the two sides of the bubble are necessary to force the bubble through the interstices between the pores. Owing to the surface tension, which tends to prevent the distortion of the bubble in passing through the pores, small globules of oil or gas will not rise through water sands under the pressure of their own buoyancy. Hence, they would not migrate until the difference of pressure on the two sides of the globule due to the hydraulic gradient was greater than the pressure due to buoyancy. Dodd in his experiments found that oil globules were forced through the sand with greater difficulty than air bubbles, and if this is the case it is evident that hydraulic currents will not cause oil globules to migrate until the difference of pressure on the two sides of the

oil globule is greater than the force of buoyancy of an air globule. It is evident, therefore, that large hydraulic gradients are required to cause the globules or bubbles to move, even in medium coarse sands, and the resistance to motion probably increases as the sands become finer.

The theory of the migration of oil due to hydraulic currents is that the surface waters enter the oil sand at an outcrop of high elevation, while water issues from the sand at an outcrop of low elevation. The difference of elevation between the point where the water enters the sand, and the point where it leaves it, divided by the distance between these points, gives the average hydraulic gradient. If, for example, a basin were 100 miles across and the outcrop of the oil sand were 1 mile higher on one side than another, the hydraulic gradient tending to cause the current would be $\frac{1}{100}$. It should be remembered that the lowest points on the outcrop of the higher side of the basin are important as well as the higher ones, for the water would tend to drain out of the low points instead of traversing the basin. If a few tight or fine bodies of sand lay in the course of the current, they would tend to reduce the hydraulic gradient of the remaining portions greatly.

There is abundant experimental evidence that, in order to move bubbles of air or globules of oil through water sands, much larger hydraulic gradients and current velocities than are likely to occur would be required. Knapp [14] has described an experiment which illustrates in a striking manner the great resistance which small masses of oil and gas offer to being propelled through water sands. Quartz sand, which had passed through a 20-mesh seive, but was held by a 40-mesh seive (diameter of grains 0.014 to 0.034 inches) was placed in a vertical cylinder $2\frac{3}{4}$ inches in diameter and 18 inches high. Water or other fluids were forced through the cylinder, the effective head on the sand being 13.2 inches. Knapp states:

> When wet sand was introduced into the cylinder, it was impossible to flow water through the sand column. The water, rising from the bottom as it was introduced from the reservoir, would drive the air, entrapped

in the sand, ahead of it until sufficient air had collected to form a series of bubbles entirely across the cylinder. Enough bubbles would usually collect about four inches from the bottom. The surface tension of the bubbles was sufficient to raise the remainder of the sand column to the top of the cylinder, and the flow of water would be shut off completely. Increasing the head to 10 feet was not sufficient to start the flow and it was necessary to agitate the sand by stirring or reversing the flow suddenly before all the air could be worked out of the sand. When most of the air had been worked out of the column, the water would flow freely through the pores. Exactly the same results were obtained when a sand wet with oil was introduced and an attempt was made to flow oil through the pores.

These observations lead to the conclusion that the failure of wells to produce oil or gas may sometimes be explained by exactly such conditions. With weak pressures, it would be possible for gas bubbles to shut off the oil flow or for even a small quantity of water bubbles in a gas sand to shut off a gas flow.

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Another experiment illustrating the resistance of globules and bubbles to motion is described by Dodd (*op. cit.*). Though the sand used in one of his experiments was rather coarse, the hydraulic gradient was ⅞ and the velocity of the water current approximately 4.3 inches per minute, a large number of globules of oil were trapped in the sand. As both the hydraulic gradient and the velocity were enormously greater than could be expected to occur in oil sands, this experiment is strongly against the theory that moving currents of water are likely to cause the migration and accumulation of oil.

As far as known there is no experimental evidence to show that oil globules or gas bubbles may be moved through oil sands by the currents of the velocity or hydraulic gradient that are likely to occur in them in nature, because the experiments relating to this question have been performed under currents and pressure gradients vastly greater than those occurring in the sands of oil fields. There is, of course, no doubt that under sufficient pressures these globules and bubbles would migrate through the sands, and Mills has described some experiments illustrating this. These experiments, however, are said to have been carried on in sands coarser than most of the oil sands of oil fields, and the velocities

and hydraulic gradients used were much greater than those likely to occur in oil fields.

While it is impossible to say exactly what the hydraulic gradients possible in oil fields would be, as they would vary in every case, nevertheless some idea of its relative magnitude may readily be obtained. Near the surface, water may move rapidly under high pressure gradients, but conditions are quite different in the case of oil sands, which must lie at considerable depths and under an impervious cover. Even if the basin were only 50 miles across, and if the effective difference of elevation between the two sides of the basin were 5,000 feet, the hydraulic gradient would only be $\frac{1}{50}$, and this is probably unusually large.

Furthermore, it seems likely that, in all except the coarser oil sands, if the pressure of the hydraulic current were sufficient to move the small globules of oil through the water sands, it would be sufficient to sweep along all larger masses of oil. Hence, no oil pools could be formed under these conditions, and any oil pools already in existence would be swept away. If, for example, the dip were 100 feet per mile, which is rather steep for the Paleozoic oil fields of the United States, if the hydraulic gradient were only $\frac{1}{100}$, and if the difference in specific gravity of the oil and water were 0.25, it is evident that no oil pools could exist. The differential head or force of buoyancy of the oil tending to oppose the hydraulic gradient would be only equal to 25 feet head of water per mile, while the force of the hydraulic gradient would be equal to 50 feet head per mile. Hence, the oil pools would be swept along with the current. In other words, the hydraulic gradient necessary to move a large body of oil, such as an oil pool, through the water sands, is so much less than the hydraulic gradient necessary to drive bubbles of gas or globules of oil through the water sands, that if the bubbles or globules were moved the oil pools would be swept away.

High temperatures and dissolved gases might enable the globules and bubbles to be moved more readily, but at the same time they would be enabled to rise more readily by virtue of their buoyancy.

If large bodies of fresh water were entering the oil sands, and coming into contact with the oil, enormous amounts of the gases would be lost by dissolving in the fresh water. The solubility of natural gas is much greater in fresh water than in salt water. Under atmospheric pressures the solubility of methane, or marsh gas, in pure water at 0 degrees Centigrade is 0.055 volumes, the solubility of ethane is 0.0987 volumes, and ethylene 0.226 volumes. These solubilities increase at a rate nearly proportional to the pressure, but are decreased by an increase of temperature, or by the presence of other gases. Substances carried down with the fresh water would be likely to combine with the oil and destroy or alter it.

Rich, in his article (*op. cit.*, p. 352), says:

> All will probably agree, also, that it (the oil) must enter the sandstone very gradually in the form of minute globules, probably of microscopic size. . . . According to the old idea of up-dip movement on account of difference in specific gravity between oil and water, the tiny oil globule will work its way up the dip of the sandstone even though the dip be as low as 10 feet per mile.

All the evidence indicates that small globules could not rise by buoyancy, but there is no necessity for assuming that they do so. There has unfortunately been a tendency to assume that oil enters the sandstones as small globules, though the writer is not aware of any satisfactory explanation of their doing so. The force necessary to drive globules of oil through water-wet shales is so enormous that it is very unlikely that such a process takes place. Moreover, even if a mixture of water and oil globules were squeezed into the oil sand, the oil globules would tend to remain where they were as soon as they entered the oil sand, and other globules would unite with them. Thus the minute oil globules would be strained out of the water until a mass had collected which was large enough to rise by buoyancy. It seems likely that the capillary force with which water tends to drive oil out of shales is less than the force required to drive oil through a water wet shale. Consequently, capillarity could not drive oil out of shales unless a joint, fault, or coarse lens penetrated the

oil-soaked shale or unless the oil shale were in contact with the oil sand. McCoy's experiment is in support of this idea. If the oil issued from the shale along joints, faults, or coarse lenses, it would enter the oil sand as a subterranean oil seep, and the oil which first entered the sand would remain near the seep until a sufficient quantity had accumulated to rise by virtue of its buoyancy. If the source rock were in direct contact with the oil sand, the oil might tend to form as a layer over the source rock, but as soon as the differences of elevation of this layer of oil were large enough, it would tend to rise by buoyancy.

If any hydraulic current through the oil sands large enough to move globules of oil or bubbles of gas through the sands were taking place at the present time, the displaced salt water would appear as enormous springs of salt water. If water were passing through a sand 50 feet thick, ten miles wide, and of 20 per cent. porosity, with a velocity of 1 foot per day, nearly 400,000 gallons of water would be displaced daily, which would have to issue up as springs.

Perhaps the most convincing proof that such hydraulic currents as required by the hydraulic theory do not occur in oil sands is afforded by the almost universal association of oil and salt water. If the fresh waters from the surface entered the oil sands in any appreciable current, the original salt water would be displaced in a short time geologically, and we would find fresh water instead of salt water in association with the oil. Waters of definite and characteristic mineral composition also occur in certain sands or at certain depths, and this relationship is contrary to what we should expect if there were even slight hydraulic currents.

Another striking fact is that accumulations of oil and gas occur where hydraulic currents are practically impossible. Faults may seal off the sands from the surface, and many sands are so lenticular that they either do not reach the surface at all, or do so only in one direction. Lenses of sandstone are reported in which gas occurs up the dip, water down the dip, and oil between the two. As these lenses have no connection with the surface, we are forced to the conclusion that the gravitative adjustment of

the oil, gas, and water in them takes place without the action of hydraulic currents, and if it can take place without them in these cases, there is no reason why it should not do so in others. Lenses of sand also occur which are entirely filled with oil or gas.

The fact that in some localities there are extensive beds of sandstone which contain no water, or are partially saturated with water, is a strong indication of the difficulty or impossibility of artesian circulation in many regions. When oil occurs in these sands it tends to occur in the synclines, or part way up the flanks of the synclines, but it should be remembered that such unsaturated rocks occur in many places in which there are no oil fields. The fact that practically no water has reached these sands during the vast stretches of geologic time is a striking proof of the fact that in many regions artesian circulation is impossible.

The theory of Mills that sudden rushes of gas towards faults have caused the accumulation of oil is subject to many of the same objections as the Hydraulic Theory. In the first place, if the oil and gas could accumulate in the unfaulted anticlines without the aid of faults, there is no need of creating a new theory to account for their accumulating in anticlines that happen to be faulted. In order to test the theory, let us attempt to determine exactly what would happen if a sand containing gas under pressure were suddenly cut by an open fault. The theory is presumably intended to explain the accumulation of oil from a disseminated condition. If the oil were already accumulated into an oil pool, all that an open fault could do is to destroy it. As already shown, it seems improbable that large amounts of oil occur scattered through the sand as globules, but for the purpose of testing the theory this will be assumed to be the case. Gas is also assumed to be scattered through the sand, either dissolved in the water or in bubbles. The events after the fault was opened up would depend largely on the hydrostatic pressure on the fluids in the sand. If the pressure were just sufficient to send up a column to the top of the anticline intersected by the fault, the pressure would not be changed any by the opening of the fault, and no

movement of oil or gas would occur. If the pressure were equivalent to the hydrostatic pressure of a column of water reaching part way from the oil sand to the surface, then on the opening of the fault a small amount of gas would expand or appear as bubbles, and force a column of water up the fault until the hydrostatic pressure of the column equalled the pressure on the sand, when motion would stop. As the volume of the water in the fault would be small, the current induced would be slight and short-lived, and the few bubbles formed would not be able to move from the point where they formed, since they could not migrate by buoyancy.

If on the other hand the original pressure on the sand were greater than that necessary to send a column of water up to the surface, then a steady flow would take place until the pressure had been diminished so that the water column no longer overflowed. Innumerable gas bubbles would form and expand, pushing out the water between them and the fault. It should be remembered that the velocity of the current would have to be vastly greater close to the fault than it would be at a distance. In fact, the case would be somewhat similar to pulling out a plug in the bottom of a tub of water. If the current were sufficient to move the oil and gas globules at a distance from the fault, close to the fault it would be many times as great as would be necessary to move them. What we would have, then, would be a current consisting of large amounts of water and gas, with some oil rushing up out of the fault. If the oil or gas united to larger masses, they would be moved more readily than the smaller masses. As these masses would be moved by the current, they could not move faster than it. As the current would be much greater near the fault, this would be the most unfavorable place for an oil accumulation to form.

SUMMARY.

Oil and gas have escaped into the source rocks from the oil sands as subterranean oil seeps. When the oil is once in the sand, capillarity and hydraulic currents are not believed to have

played an important part in its migration. Where very fine sands and medium or coarse sands occur together, capillarity may cause the oil to occur in the coarser, but the vertical adjustments caused by this force can not be large in medium and coarse sands. The oil entering the sands accumulated in place until it could migrate by buoyancy, when it gradually threaded its way up the dip towards an anticline or other trap.

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NOTES ON GROUND WATERS.[1]

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I SHALL not pose as an authority, but shall treat of a few specific occurrences that involve (1) deviation from the general relation between ground water surface and land surface, (2) the lower limits of ground water, (3) changes in ground water level during Tertiary and Quaternary time, and (4) the chemical work of ground waters. I hope that others, here or hereafter, will contribute much more to the subject.

1. *Local Deviations from the General Relation between Ground Water Surface and Land Surface.*—It is generally stated that the ground water surface fluctuates in the same direction as the surface of the land, but to a less degree. The degree depends upon the supply of rain water, the uniformity and permeability of the rocks, and the topographic relief. If we assume a permeable rock of uniform character the curvation of the water table depends upon the rate at which water can reach the level of the valley. If new supplies arrive as fast as the water can move downward through finely porous material the water table nearly coincides with the land surface the only difference being due to evaporation between rains. If the supply is less or the pores larger and more abundant the table is lower and lower approaching the valley level as a limit. This ideal condition is subject to endless variation if differences in texture and structure of the rocks are considered. In crystalline, or uniformly impervious siliceous rocks, water moves principally along the more open fissures. There is no definite water table, but the depth to ground water again depends upon the ratio of supply to downward movement, and is believed to vary in a general way with the land surface. Two exceptions to these general relations are found in

[1] Presented before the Society of Economic Geologists, New York Meeting, May, 1923, to initiate a discussion on the relation of ground waters to ore deposits.

[2] Published by permission of the Director of the U. S. Geological Survey.

the Tintic mining district, Utah, and the Leadville mining district, Colo.

In the Tintic district the higher ridges consist of very steeply dipping limestone which continues beyond the deepest workings. The lower slopes to the southwest consist of intrusive monzonite. A few shafts in the monzonite tapped water at depths ranging from 100 to 500 feet.[2] More data might show a generally normal relation to the topography. In the higher limestone ground, however, the water is at a much lower elevation than in the monzonite. The Dragon shaft in limestone near the monzonite contact is 1,000 feet deep and a vertical drill hole from its bottom extends 800 feet farther before reaching monzonite. Both shaft and drill hole were dry, but drifts into the porphyry tapped strong flows of water in fissures on the 800 and 1,000 foot levels. These levels are lower than the water level in the Sunbeam mine, although the land surface is higher, and are much higher than the water in the nearest mines in limestone. Water in the limestone is not at a uniform level, but the general level is not far above that of Utah Lake 15 miles to the northeast, the only body of fresh water in the region.[3] The widening of fissures by solution has evidently allowed water to descend rapidly until it has reached the approximate base level of underground flow and shows no relation to the topography.

In contrast to the Tintic district certain small districts 20 to 30 miles farther west have very shallow ground water levels, although the climate is equally dry in both places. The prevailing rocks are mostly quartzite with intercalated beds of shale, and locally granite. My impression after a reconnaissance of these districts was that siliceous rocks in which fractures were not subject to appreciable enlargement by solution but subject to some tightening through kaolinization retarded the downward movement of water with corresponding shallowness of the water table and parallelism between it and the ground surface.

The Tintic Standard mine in the East Tintic district, however, has penetrated considerable shale and quartzite below the

[2] See Fig. 16, U. S. Geol. Surv. Prof. Paper 107.

[3] See Fig. 3, *Idem.*

limestone, and its lowest workings must be close to the level of water in the deep mines three miles to the west; but it is very dry except for a little seepage along certain shale beds. The ore-bodies of the mine lie in a down-faulted trough-shaped block where the quartzite and shale, rendered comparatively brittle by silicification, are so shattered that water can percolate downward more rapidly than usual. The mine is dusty and hot, due to rapid oxidation of sulphides. The heat causes rapid evaporation and drift walls are thickly coated with sulphate efflorescences, which lose at least part of their water of crystallization with comparative rapidity. The local supply of water, therefore, is partly consumed by formation of hydrous sulphate and partly by evaporation and removal to surface by ventilation. A local pocket of mineralized water was tapped in a winze at the bottom of the mine, and will be referred to later. The main body of ground water is presumably only a short distance lower.

Near the Tintic Standard mine there are a few springs emerg-

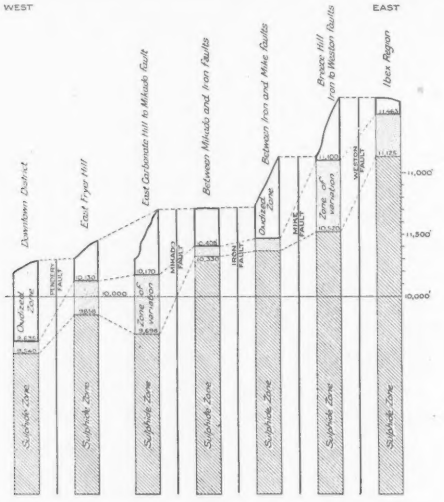

FIG. 7. Diagram showing depths of complete oxidation and tops of sulphide zones in fault blocks of Leadville, Colo.
(By J. D. Irving.)

ing from rhyolite which overlies the limestone of the region. These springs represent water that can not percolate downward into the limestone as fast as it is supplied at the surface. In other words there is a shallow body of ground water in the overlying volcanic rocks, and a deep body in and below the underlying limestone.

In the Leadville district ground water is separated into a number of basins or reservoirs which are bounded by the principal post-mineral faults. The original water levels are now largely destroyed by drainage and pumping, and their approximate positions are indicated by the lower limits of oxidation. The greater elevation of these reservoirs from west to east corresponds with the general rise of the land surface, as shown in Fig. 7; but within any reservoir there is considerable variation in the depth to ground water, and the lower limits of oxidation approach a horizontal plane or tend to conform to the dip of the limestone strata, which is about 20° eastward. The fault zones themselves are small reservoirs of intermediate altitude. The margins of gouge along the faults are effective dams. Water working downward slowly through the overlying porphyry could descend rapidly along the Blue limestone and also along the White limestone after penetrating the Parting quartzite with its shaly beds. The Cambrian quartzite with its upper shaly member and the basal granite effectively retarded further progress downward except along faults and occasional open fissures. The enlargement of openings in the limestone permitted the water table to become approximately horizontal, or even to slope eastward because of circulation along the limestone beds. Only where there were leaks in the gouge walls of the faults could appreciable quantities of water pass from one reservoir to another.

The amount of oxidation that has taken place in a fault block varies according to the kind of rock. In the overlying porphyry it is confined to slight depths except along fissures, and gives the impression of a very shallow water table; but directly under it in the limestone, oxidation may be extensive and complete, and its lower limit is approximately horizontal. Conditions within a fault block, therefore, are similar on a small scale to conditions

in the Tintic district; where the abundance and size of openings permit, water quickly attains its local base level regardless of the topography.

LOWER LIMITS OF GROUND WATER.

The foregoing considerations of the downward movement of ground water raise the question as to its lower limits. I have never had an opportunity for detailed work in districts where mining has passed below the limits of the natural free circulation of water, and I hope that those who have will supply information on this subject. It would appear that with increasing depth joints become tighter and tighter and that even major faults tend to close, although local openings in them may persist to great depth. Water therefore is prevented from circulating downward at an appreciable rate unless the texture of the rock be sufficiently porous. In impervious rocks the general lower limit is a few hundred feet below the surface. In porous rocks which are not sealed off from the surface by impervious strata circulation may continue downward indefinitely, as the pores would not be closed by pressure at less than 10 or 15 miles in depth.

Anomalous dry sandstones have been cited, but it is interesting to note from a few interviews that at least some geologists best qualified to express an opinion do not accept this anomaly. They believe that the sandstones will prove on examination to be less porous than supposed, or that the sealing of the beds between impervious strata prevents appreciable circulation.

CHANGES IN GROUND-WATER LEVEL DURING TERTIARY AND QUATERNARY TIME.

The best known examples of changes in water level are in certain copper mines in Arizona, where discrepancies between the depth of oxidation and the present water level favor the conclusion that ground water was formerly at a considerably lower level than at present. In the Chief Consolidated Mine, Tintic district, Utah, thorough oxidation has been reported to exist well below the present water level, and points to the same conclusion.

In the Leadville district, which is in a humid region today,

there is similar evidence. In the Downtown or western part of the district, when pumping was suspended during the great strike of 1896, water rose to a level about 375 feet above the lower limit of pronounced oxidation, which is 740 feet below ground surface and 450 feet below bed rock surface; but this may have been above the original level, as some connections had been made with the higher reservoir to the east. In this higher reservoir, beneath Carbonate Hill, the bottom of oxidation in the Maid Mine is at an altitude of 9,980 feet above sea level, or about 565 feet below the surface which for the most part coincides with the bed rock surface. It is reported that water would rise to about 265 feet above this depth if pumping ceased; but since pumping ceased in 1919 water in the Mikado shaft, farther east in the same fault block, rose to an altitude of 10,085 feet (March, 1922), or 105 feet above the bottom of oxidation, and has undergone little change since.

More reliable data are available for the East Fryer Hill area where water level has not been appreciably affected by changes in other parts of the district. Here the depth of oxidation except in the Hayden shaft averages about 400 feet from the ground surface and a little more than 300 feet below bed rock surface. J. D. Irving, who compiled most of the foregoing data, noted that the thickness of glacial debris in the East Fryer Hill area was about equal to the height of the water table above the top of the sulphide ores. With allowance for disturbances of water level by mining operations similar approximate relations exist in the Downtown and Carbonate Hill areas, and Irving, therefore, has suggested that deposition of glacial debris, which is an excellent water catcher, accounts for the rise in water level.

In the northeastern part of the district, however, this explanation is inadequate. There, glacial deposits, except lateral moraines, are negligible and there was considerable erosion by the Evans Gulch glacier. Water level, where not lowered by drainage into the Yak tunnel, is shallow, but the lower limit of oxidation attains considerable depth and is quite independent of the topography (see Fig. 8). Where glacial erosion has removed

some of the limestone oxidation has a minimum depth of 25 feet below bed rock surface and 75 feet below ground surface. Where the limestones are covered by porphyry or the Weber formation the depth of oxidation increases with the northeastward dip of the strata until in the Resurrection, Sadalia, and Diamond

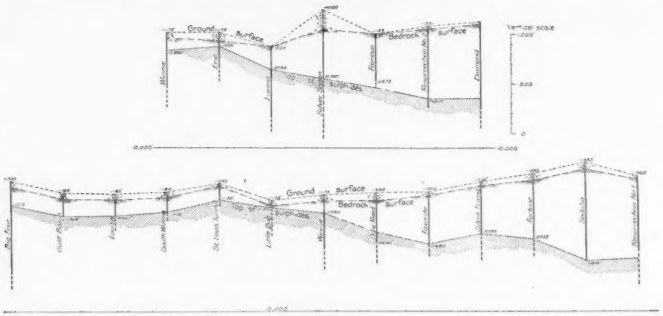

FIG. 8. Discordant relations between ground surface and depth of oxidation in upper Evans gulch area, Leadville, Colo
Glacial moraine overlies bed rock
(By J. D. Irving.)

mines it is about 900 feet. Oxidation evidently took place where water could circulate most freely, along the Blue limestone between an impervious roof of porphyry or shale, and an impervious floor of shale at the top of the Parting quartzite. The discrepancy between this relatively great depth of oxidation and the water level before its disturbance by mining operations is too great to be accounted for by glacial deposition, and indicates that water level was formerly much lower.

Irving, from his study of the district, concluded that by far the greatest amount of oxidation took place prior to any glaciation, that is, in late Tertiary time. The region characterized by a lower water level in Tertiary time than at present therefore appears more extensive than has been realized, and the correlation of ground water level in Tertiary and Quaternary times may deserve a more general study than it has received.

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CHEMICAL WORK OF GROUND WATERS.

To this large and complicated subject I shall contribute one or two items which have particularly interested me. I have already mentioned the pocket of water found in the bottom of the Tintic Standard mine in 1922. This water, according to James Wade, Superintendent, accumulated in a winze from the 1,450 foot level for 3 days, and when found it was coated by a yellowish scum. Analysis of the scum by the company's chemist is given in Column I.

I			II	
Insoluble (Silica)	38.4	33.0	Assumed compounds.	
Alumina	11.7		Zinc sulphide	6.7
Iron (Fe)	10.7		Iron disulphide	42.2
Zinc	4.5		Excess sulphur	.8
Sulphur	25.5		Silica and Alumina	50.1
Silver		4.0 oz.		99.8
Lead	None			
Copper	Trace			
Arsenic	None			
	90.8			

Recalculation of the analysis is shown in column II. There has been no opportunity to study the material, as none of it was preserved, and the identity of the zinc and iron sulphides can not be determined. It is worth while, however, to recall the rich silver ore in the Gemini Mine (Tintic district) containing pearceite, spherulitic zinc blende and marcasite, and small, clear crystals of quartz, in addition to the more characteristic ore and gangue minerals.[1] Lindgren concluded that this ore was formed by relatively cool solutions, ascending or descending, which had increased their silver content by traversing ores of medium richness. The water in the Tintic Standard differs from these solutions in its low content of silver and absence of arsenic, but is similar in its content of zinc and iron sulphides, and suggests that those minerals in the Gem Channel were deposited by descending waters in which sulphates had been reduced to sulphides.

[1] Lindgren, W., and Loughlin, G. F., "The Geology and Ore Deposits of the Tintic Mining District, Utah," Prof. Paper 107, U. S. Geol. Survey, pp. 179–180, 1919.

Butler has described the wurtzite in the San Francisco district as a deposit from descending waters, and some of the ores from the Little Annie and other mines at Aspen, Colo., contain fine druses of zinc blende distinctly later than the other sulphides and gangue. These two forms of zinc sulphide also may have been deposited by descending sulphide solution similar in general to that in the Tintic Standard mine, though differing from each other in some respects. Such deposits as a whole, however, appear to be scarce.

Whether the "insoluble" in scum on the Tintic Standard water was originally in suspension or in solution is not known. The ratio of silica to alumina could be interpreted as one or more of the hydrous aluminum silicates, kaolinite, leverierrite, and montmorillonite, with some excess silica. The largest masses of such clay minerals, collectively called kaolin, in the Tintic district are now in the oxidized zone, but are interpreted as replacement deposits from descending waters. Those waters in the lower parts of their courses may have resembled[2] the Tintic Standard water, although the brown iron ore which formed after the kaolin had replaced parts of it must have been deposited from sulphate rather than sulphide waters.

The kaolin in certain sulphide ores in the Leadville district is of particular interest in this connection. It has been noted in different parts of the district but the most interesting occurrences were found in the Golden Eagle mine, Breece Hill. The sulphides, principally pyrite and chalcopyrite, are either tarnished and coated with films of chalcocite, or are free from any sign of alternation; but the original gangue, manganosiderite, is almost completely replaced by kaolin. Where replacement is complete the sulphides show no evidence whatever of mechanical disturbance and in part no evidence of chemical reaction. Where the sulphides are coated with chalcocite the chalcocite has been deposited later than the kaolin, and apparently represents a later stage of alteration. The ore is on or below the seventh level from the Ibex No. 2 shaft and is well below the original ground

[2] *Idem.*, pp. 258–265.

water level. Certain beds of the White limestone are also replaced by kaolin. Evidently water that descended through a considerable volume of pyritic porphyry had dissolved alumina and silica and carried them to or below water level, where local impounding between impervious shale beds or porphyry sills and the presence of carbonates favored deposition by replacement.

Kaolin is so commonly regarded as a residual mineral that some emphasis on its deposition by replacement at or below the bottom of the oxidized zone is merited. The constituents of kaolin in the water of the Tintic Standard mine lend further emphasis. It is regretted that complete analysis of this water and its scum were not made, but the significance of the occurrence was not appreciated when the water was found, and no occurrences have been found since.

These specific occurrences raise the question as to how much we know about the composition of ground waters unaffected by mining operations, either below water level or after their content of oxygen has been exhausted. We can study the results of their reactions as revealed in mineral deposits, but more samples of water need to be collected at points where new bodies of water are tapped and before they can be appreciably affected by contact with the mine's atmosphere. Such opportunities are few but we should make the most of them.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. D.

POSSIBLE POTASH PRODUCTION FROM MINNESOTA SHALE.

HARRISON A. SCHMITT.

IT has been known for several years that a certain shale in the State of Minnesota carried an exceptional amount of potash,[1] and the present paper is concerned with the problem of whether this shale has any commercial value because of its potash content, aside from its value for brick manufacture.

In connection with this work the writer is greatly indebted to Dr. F. F. Grout and Dr. W. H. Emmons of the Department of Geology, to Dr. I. W. Geiger of the Department of Chemistry, and to Dr. F. J. Alway of the Department of Agriculture, of the University of Minnesota for criticisms and suggestions.

THE DECORAH AND GALENA FORMATIONS.

The particular shale in Minnesota known to have a high potash content, the Decorah shale, has the position given below in the Ordovician section as found in Minnesota.

6. Galena limestone
5. Decorah shale
4. Platteville limestone
3. St. Peter sandstone
2. Shakopee dolomite
1. Oneota dolomite.

The Galena limestone directly above the Decorah has many potash rich shale layers.

The outcrop from which most of the shale samples were taken is part of an erosional outlier located at Cherokee Heights, St. Paul. Here the shale outcrops for several miles along the Mis-

[1] Grout, F. F., "Clays and Shales of Minnesota," U. S. Geol. Survey Bull. 678, p. 152.

sissippi River. The whole area, including that in which the shale outcrops and that in which it is drift covered, is in a part of the State that is well farmed, thickly populated, and readily accessible by a network of railways and good roads.

The Decorah formation at St. Paul has a thickness of about 60 feet, 50 feet of this being green-clay shale and 10 feet of limestones low in magnesia. The limestones are in thin lenticular layers, that increase in thickness and number toward the top until they merge into the Galena formation.

The Decorah is everywhere color-banded but is not laminated or fissile except along some calcareous layers. When fresh it is green but it weathers to buff or brown. On exposure it breaks with a cuboidal fracture and weathers to clay in a single season.[2]

The Galena formation, only 40 feet thick here, has much the same character as the upper part of the Decorah where the limestone lenses are thicker. In the Galena, the limestones make up about 50 per cent. of the formation; the other 50 per cent. being shale of the same character as that in the Decorah and with a similar high potash content.

SAMPLING THE DECORAH AND GALENA FORMATIONS.

Three channel samples were taken of different successive parts of the geologic section. The samples were numbered 3, 4, and 5. Proportional parts of these samples were mixed to make a sample (number 6) representing the entire part sample, about 84 feet of vertical section. The analyses of these samples are given in Table I.

FORMER WORK ON POTASH IN SHALES.

Previous experimentation with clays and shales for potash extraction has been along the following lines:

1. Extraction of potash from flue dust of cement kilns.

2. The Cowles process (patented) designed to extract alumina from clay, with hydrochloric acid and potash as by-products.[3] In

[2] Sardeson, F. W., U. S. Survey Folio 201, Minneapolis, St. Paul.

[3] Phalen, W. C., "Mineral Resources 1915," U. S. Geol. Survey, pt. II., p. 115. Also see U. S. patent 1,111,881.

this process a mixture of salt and clay is pressed into briquettes and heated in the presence of superheated steam, whereby HCl is given off and alkali-silico-aluminate formed; this compound is then decomposed by heating with limestone to form lime silicate, a soluble alkali-aluminate being left.

TABLE I.

ANALYSES OF SAMPLES OF DECORAH AND GALENA FORMATIONS.

	3	4	5	6
SiO_2		38.37	53.93	37.87
Al_2O_3		22.06	13.88	14.23
Fe_2O_3				2.97
FeO				1.63
MgO		5.77	4.05	3.29
CaO		10.87	20.98	14.73
Na_2O				.43
K_2O	8.24	6.44	5.04	5.96
H_2O+		16.50	19.58	2.67
H_2O-				1.25
CO_2				13.94
TiO_2				.45
P_2O_5		3.47	2.85	2.83
S		.10	.10	.10
		100.36	99.75	99.80

3. In a process outlined by A. W. Heyman,[4] a calcareous mixture (containing potash in clay, shale, orthoclase, etc.), either natural or artificial, is heated to 900–1600° C. The hot material, or the ground cold material, is treated with water and the hydroxide of potash extracted from this solution. The residue may be used for cement manufacture.

4. Clay, salt, and calcium carbonate when heated together give water soluble potash.[5]

5. U. S. patent 521,712. Clay $(NH_4)_2SO_4$ and K_2SO_4 are heated together and the potash leached from the frit.

[3] Lower ten feet of the potash shale.

[4] Intermediate thirty feet.

[5] Upper forty-four feet.

[6] Representative sample of whole section, eighty-four feet.

[4] Phalen, W. C., "Mineral Resources 1915," pt. II., p. 121.

[5] Chem. Abs. 13, p. 1625. See also U. S. patent 1,297,078.

6. U. S. patent 1,123,693. Feldspar and clay are heated in the presence of NaCl and H_2O. Soluble K_2O is extracted.

7. U. S. patent 1,236,903. Slate, shales, etc., are furnaced with limestone and the potash volatilized.

8. The study of the availability of potash in shales for plant food.[6]

Published work on potash extraction from silicate rocks has shown the following results:

1. Potash recovery from cement manufacture has been a commercial success and possibly will continue to be, depending somewhat on the price of potash.

2. Methods of extraction of potash from silicate rocks primarily for recovery of potash, and with no byproduct produced, have been of doubtful value except possibly during the past period of high potash prices.

3. High potash shale may make a valuable fertilizer. Preliminary pot tests show excellent results,[7] but, for reasons later discussed, preliminary field tests show negative results.

4. Under certain conditions, when lime is intimately mixed with a silicate carrying potash, and heated, an exchange of bases occurs, potash being released from its previous combination. This point is fundamental and the basis for many processes of potash extraction.

5. Concentrated H_2SO_4, HF, and other acids will decompose certain silicates containing potash, the potash becoming soluble in the acid.

6. Pulverizing and heating makes some potash water soluble in rocks such as alunite.[8]

7. Water and CO_2 under high pressure and temperature decompose some silicates.

Many processes for potash extraction from silicate rocks (including clay, shale, slate, and phyllite) are based upon one or more of the above reactions.

[6] Austin, M. M., and Parr, S. W., "Potash Shales in Illinois," *J. I. E. C.*, vol. 13, pp. 1144–1146.

[7] Univ. of Ill. Agric. Exp. Station Bull. 232, p. 229.

[8] Nourse, M. R., "Mineral Resources 1920," U. S. Geol. Survey, pt. II., p. 106.

SELECTION OF PROMISING PROCESSES.

After preliminary experimentation and after a survey of the literature on potash extraction by commercial or possible commercial methods, certain lines of attack were selected.

1. The possibility of using the shale as fertilizer.

2. The possibility of using the shale in a portland cement mixture.

3. Special processes for potash extraction.

a. Volatilizing or dissolving potash from a heated mix of shale, NaCl and $CaCO_3$.

b. Using the same materials and attempting to obtain brick as a byproduct.

c. Experiments with CaO, shale, and water under pressure and heat with the idea of obtaining KOH and also a lime residue for use in making sand lime brick as a byproduct.[9]

USE OF THE DECORAH SHALE AS FERTILIZER.

Preliminary pot tests by the Agricultural Experiment Station of the University of Illinois showed that the potash content in a certain Illinois shale gave phenomenal results as a fertilizer.[10] Some of the potash in the shale, though it was not water soluble, was evidently more available for plant food than the water soluble potash in commercial fertilizer. Field tests made with this Illinois shale showed negative results.

There is close correspondence between the per cent. of K_2O soluble in sulfuric acid in the Illinois and Minnesota shales. In the latter, 60 per cent. of the total potash is in soluble concentrated H_2SO_4.

This suggests that some of the potash in the Minnesota shale may be in the same combination as in the case of the Illinois shale. Therefore, it is believed that the Minnesota shale will not only show beneficial results as a fertilizer in pot tests, as did the Illinois shale, but will have certain advantages for field use not obtained by the Illinois shale.

[9] Charlton, H. W., "Recovery of Potash from Greensand," *J. I. E. C.*, vol. 10, pp. 6–8.

[10] Austin, M. M., and Parr, S. W., Univ. of Ill. Agr. Exp. Sta. Bull. 232.

There are certain difficulties connected with the use of the Illinois shale, chiefly that it is thin, low in potash, and does not slack.

In contrast, the Decorah shale has these advantages:

1. It is easily pulverized.
2. It slacks on one season's exposure, consequently grinding might be eliminated.
3. Its potash content is over 8 per cent. in one 10-foot layer, while the whole thickness of 100 feet carries nearly 6 per cent. K_2O.
4. It contains considerable limestone which would have a value as fertilizer for lime deficient soils.
5. The formation is extensive, thick, and easily available.
6. It is near great acreages of potash deficient peat soils.

It is noteworthy that peat soils are not only usually deficient in potash but also deficient in clay.

If 60 per cent. of the potash of the potash rich shale were available for plant food, a dressing of one ton of shale to the acre would be equivalent to a top dressing of 175 pounds of 80 per cent. muriate. This is a little more muriate than is usually applied.

AVAILABILITY OF DECORAH SHALE FOR A PORTLAND CEMENT MIX.

In American practice a shale or clay is considered suitable for cement manufacture when the silica-alumina ratio falls between 2.5–3.5.[11] The ratio for the Decorah shale is 2.8 for the lower layers of the formation.

If limestone three times the weight of the shale is considered necessary to compound a suitable cement mix, on the basis of a 66 per cent. recovery from the shale in the lower layers, the recovery per barrel of cement would be 5.28 pounds in comparison to 2.9 pounds, the average recovery for American practice. If the shale represented by sample number 3 were used, the recovery of potash would be correspondingly higher.

[11] Austin, M. M., and Parr, S. W., Univ. of Illinois Agr. Exp. Sta. Bull. 232.

There is a remote possibility that the Devonian in the south part of the State contains commercial quantities of cement rock. If such a deposit exists and a cement industry could be located there, the Decorah shale could be profitably used in the cement mix. The shale outcrop is only a short distance from the Devonian. Lake marls, known to be suitable for portland cement, are found in the State.

EXTRACTING POTASH FROM THE CALCAREOUS SHALE MIXED WITH SODIUM CHLORIDE.

Figures 9 and 10 show the amount of extraction of potash in per cent. where the amount of shale and $CaCO_3$ are the variables and the amount of NaCl is constant. One curve shows the amount of potash (K_2O) made water soluble at 800° C. while the other shows the amount volatilized at 1150° C.

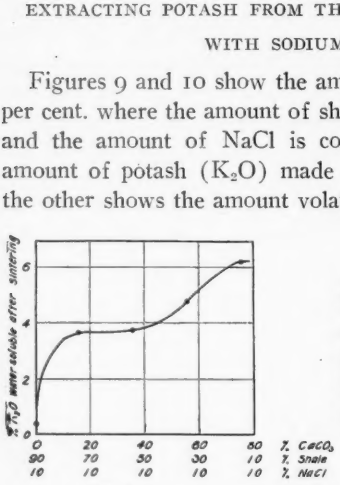

FIG. 9.

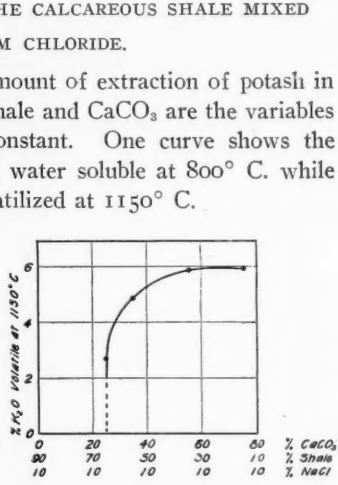

FIG. 10.

Curves showing in per cents. the amount of potash water soluble after sintering at 800° C. (Fig. 9) and the amount volatile at 1150° C. (Fig. 10) with varying proportions of shale and $CaCO_3$. The NaCl kept constant.

It was later found that the results shown by the curves could be obtained by using much smaller amounts of NaCl. The amount of NaCl equivalent to the amount of K_2O present plus a slight excess is sufficient to free the potash.

However, these curves do show the intimate relation of the per cent. of potash extraction to the per cent. of $CaCO_3$ present. The "flattening" out of the curve in Fig. 9 is probably due to

the fact that the potash is held in two combinations, one of them more resistant to decomposition than the other.

Fusion occurs where the $CaCO_3$ is below 25 per cent. and the temperature above 1150° C. The writer is of the opinion that the downward break in the curve for volatile potash, which is apparently due to fusion, could be somewhat flattened out by heating at a slightly lower temperature for a longer period of time. This was actually done with samples number 4, 5, and 6, increasing the amount of volatilization above that shown by the curve. The following table gives (1) the per cent. of $CaCO_3$ in each sample, (2) the per cent. of K_2O in each sample, (3) the per cent. of NaCl used, (4) the volatilization estimated by reference to the curves, (5) the actual volatilization obtained by experiment, and (6) the per cent. efficiency of potash volatilization.

Sample.	1. $CaCO_3$.	2. K_2O.	3. NaCl.	4. Estimated Volatilization.	5. Actual Volatilization.	6. Per Cent. Efficiency of Volatilization.
4	19.40	6.44%	10%	0.00%	3.26%	50.62%
5	37.45	5.04	10.	4.18	5.04	100.00
6	26.29	5.96	10.	3.36	4.81	80.70

Sample number 5 gives complete volatilization. Under carefully regulated conditions of mining and milling the volatilization efficiency of the material represented by sample number 6 could also be brought to 100 per cent. Thus, in mining it would be simple enough to mine some of the Platteville limestone along with the Decorah and Galena formations and thus increase the $CaCO_3$ content. In some places the amount of included limestone is greater and perhaps additional limestone would not be needed to obtain complete recovery.

Though no quantitative analyses of the sublimates from the above mixtures were made, qualitative tests showed that some potash came off as KCl with some NaCl and possibly some K_2O. In any event, all the sublimate is water soluble and rich in potash.

The stripping and mining of the shale could be done by steam shovel for large scale operations, and in the milling the salt could

be added in the ball mill, thus causing intimate mixing and grinding.

The sintering process might present a difficult mechanical problem but it is probable that a suitable continuous process furnace could be designed. The sublimate should be led off, out of contact with the flue gases, so the standard portland cement kiln would possibly not be satisfactory. However, an impure product could be obtained with the standard kiln.

The calculated composition of the tailings is as follows: It is based on the processing of representative sample number 6. Na_2O is considered replacing K_2O. Sulphur may or may not be lost on sintering.

SiO_2	47.29	H_2O-	0.00
Al_2O_3	17.75	CO_2	0.00
Fe_2O_3	5.97	TiO_2	.56
MgO	4.10	P_2O_5	.35
CaO	18.40	S	.12
Na_2O	5.43		
K_2O	0.00		99.97
H_2O+	0.00		

If the process could be so regulated that the tailings could leave the furnace in an agglomerated condition they could be used as road material or cement filler, otherwise their disposal would be an item of expense. It is noteworthy that at several places in the West, where there is a distinct lack of sand and gravel, fused or agglomerated shale is used as a substitute,[12] being made in a standard portland cement kiln. The byproduct of the potash extraction process is a similar material.

The amount of the product, on the basis of volatilization of all the potash from representative sample number 6 using 10 per cent. added limestone, would be 5.41 per cent. of the raw material treated. This would be equivalent to the production of 215 pounds of 80 per cent. muriate[13] per short ton of shale treated. Based on prices for muriate existing from 1911–1914 this amount would have a value of about $5.20 f. o. b. St. Paul, Minnesota. This is the gross value of the product per ton of shale and limestone treated.

[12] The Midwest Refining Co., Salt Creek, Wyoming.

[13] The standard concentration of muriate. The other 20 per cent. is NaCl.

POTASH EXTRACTION WITH BRICK AS A BY-PRODUCT.

It was thought that perhaps by taking advantage of the water soluble and volatile features where NaCl was added to the calcareous clay, bricks could be made, and that either water soluble potash could be leached from the finished product, or that the bricks could be burned at a temperature sufficiently high to volatilize all the potash. Some preliminary tests show that where a high lime content is present (10 to 20 per cent. CaO) satisfactory brick of common building grade can be produced only at about 800–900° C. Further, it was found that a combination of the water soluble and volatile methods would give the greatest efficiency of extraction at the temperature burning the best brick (between 800° and 900° C.). Within this temperature range some potash would be volatilized, but some would remain water soluble in the brick and could later be leached from the cooled brick.

Briquettes were made from each of the samples 4, 5, and 6. During the mixing, 10 per cent. NaCl was added to each sample, both the NaCl and the samples having been ground to an impalpable powder. Only just sufficient water was added to make the clay plastic in order to prevent efflorescence of the NaCl during drying.

Three briquettes were burned for each sample with the following results:

Temperature Centigrade.	Color.	Remarks.	K_2O.	
			Volatile.	Soluble.
		Sample No. 4		
750	Salmon	Fair common grade		
850	Do.	Do.		
1110	Buff	Incipient fusion		
		Sample No. 5		
750	White	Good common grade		
850	Salmon	Do.		
1110	Buff	Incipient fusion		
		Sample No. 6		
750	White	Poor common grade		
850	Salmon	Good common grade	.....	....2.91
1110	Buff	Incipient fusion.....	....3.46	

BOMB TESTS WITH SHALE AND LIME MIXTURES.

Harlton[14] placed greensand, CaO and water, in certain proportions, in an autoclave and brought them to high pressures and temperature. The potash in the greensand became water soluble in the form of KOH and could be filtered from the sludge.

This experiment was duplicated, substituting shale for greensand. The proportions of the constituents were the same as those recommended as most favorable for greensand, viz., shale 1 part, CaO 0.9 part, and water 5 parts. The temperature was 238° C. giving a pressure of 438 pounds per square inch in the bomb. The time of heating was four hours.

On testing the residue it was found that the extraction in one case (the highest) was 3.5 per cent. K_2O or 56 per cent. of the total potash present.

Since in this case the shale had not been previously finely ground and some of it was still in lumps on opening the bomb, and since there was evidently not enough water present, for the residue was dry, it is thought that by using finely ground shale and by increasing the water content the extraction could be considerably increased.

If this method were used for potash extraction and the sludge were suitable for sand-lime brick manufacture, the St. Peter sandstone would be an excellent source for the sand used in the brick. This sand has long been used for satisfactory sand-lime brick.

CONCLUSIONS.

The Decorah shale in Minnesota is an extensive potash rich shale (6 to 8 per cent. K_2O).

The potash is in two states of combination; about 60 per cent. of it more easily available than the rest.

Much potash can be obtained from this shale by heat treatment with sodium salts equivalent in amount to the K_2O and with a slight excess of $CaCO_3$

[14] Harlton, H. W., "Recovery of Potash from Greensand," *J. I. E. C.*, vol. 10, pp. 6–8.

The potash in the Decorah shale can be rendered soluble and volatilized in part from bricks where salt and $CaCO_3$ have been added to the raw shale.

The Decorah shale is favorably situated for use with sand if a by-product from potash extraction is suitable for sand-lime brick as in a greensand process already patented.

The Decorah shale is also situated near some limestone which may be suitable for portland cement. The Decorah is probably suitable for use in a cement mix.

The Decorah is being tried, without preliminary heat treatment, with considerable promise of success, as a fertilizer for potash deficient peat soils which are common near some of its outcrops.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

EDITORIAL

THE EÖTVÖS TORSION BALANCE

It was with no small interest that we published in the second last number the article by Stephen Rybar on the Eötvös torsion balance. We regret that the article could not receive earlier publication due to the delays caused by the necessary revision of a manuscript submitted by one writing under the handicap of the lack of thorough familiarity with the intricacies of the English language.

The importance of this means of investigation has already become apparent to petroleum geologists, but to our knowledge it has not as yet been applied to ore deposits. Here then lies a new field of investigation in the search for ore bodies—a method that has had already the test of considerable field work, in which there has been shown a discriminating distinction of surprising delicacy between heavier and lighter masses. There is no witchstick taint to this method; it is based on sound scientific principles—principles well known to the geodesist. Nor is there the drawback of the criticisms that have been made of many of the electrical methods of outlining ore bodies, though the practical utilization of the Eötvös instrument does appear formidable, and has drawbacks of another character. For example, the operator must be able to use higher mathematics and the field work must be preceded by a course of instruction in the use of the intricate formulæ. Another drawback lies in the sensitiveness of the instrument to adjacent topographic features. Consequently the best results may be obtained only in flattish regions. It is possible that satisfactory results may not even be obtained by surface work in mountainous regions of high relief and rugged topography.

The full description of the Eötvös method is timely in view

of the discussions familiar to all of us of late regarding the lack of new discoveries of mineral deposits. And in no less degree has the problem of finding new ore bodies in old mines been occupying the thoughts of economic geologists. It is now generally recognized that future additions to our mineral resources must depend in large part upon more careful, more elaborate, and more scientific methods of exploration than have been employed in the past. The Eötvös instrument may afford the means of removing much of the haphazard from the present costly and wasteful methods of mineral exploration. Its utilization for mining work does not appear impracticable nor the difficulties of handling it insurmountable. The drawback of rugged topography might be overcome by using it in underground workings such as tunnels, drifts, or cross-cuts, where the influence of immediate topographic relief would be almost entirely eliminated and where temperature changes would be negligible. It should yield more striking results where applied to masses of high specific gravity such as ores, than with the materials on which it has already been tried.

We take this opportunity, then, to direct attention of economic geologists to the possibilities of the Eötvös torsion balance in the search for new ore bodies—possibilities that may prove of far-reaching importance in the discovery of new ore deposits for the future. But it can not be used indiscriminately for outlining any class of ore deposit. The instrument depends for its results upon the difference in gravitative pull exerted upon it by heavy bodies as contrasted with light bodies. Therefore, it is evident that satisfactory results could be obtained only in the case of ore bodies whose specific gravity is appreciably higher than that of the enclosing rocks. Consequently its use in mining geology is restricted largely to those deposits of some size in which the heavy ore minerals constitute an appreciable part of the ore. This calls to mind deposits of iron ore and chromite, or bodies of massive sulphide, or veins or shear zones highly charged with heavy minerals, or other similar classes of mineral deposits. It is possible that results might be obtained from large

bodies whose specific gravity is appreciably less than that of the enclosing rock. For example, big masses of gold quartz relatively free from sulphides and enclosed in a heavy basic igneous rock.

On the other hand it would be futile to experiment with the Eötvös instrument on deposits whose specific gravity is practically the same as that of the surrounding country rock. In this class would fall a great number of ore deposits such as quartz bodies in acidic igneous rocks, narrow veins, many non-metallic mineral deposits, lightly impregnated shear zones, or the group of "porphyry" deposits in which the disseminated sulphides form but a small part of the rock. Many oxidized deposits would also give little contrast in specific gravity. This is also true of a great number of those ore deposits whose value depends upon the winning of an insignificant weight of a high-priced metal, such as gold.

There remain, however, many classes of deposits for the exploration of which the Eötvös torsion balance may prove of great value; it may be the threshold of a new era of scientific prospecting.

ON INTRODUCTIONS

When a reader surrounded by more literature of his subject than time will permit him to read, and in a critical attitude as to what he will read, leafs over the pages of a journal, a pleasing introduction may catch his eye and whet his appetite to read more. It is perhaps one of our present-day misfortunes that scientific literature is so voluminous that we all can not read everything. In consequence there has developed in us a pick and choose attitude in order that we may conserve somewhat our precious time for the specialties that interest us most. The wary reader, therefore, has to be enticed to read and a good introduction to an article may offer the necessary incentive to lead him on.

We may take it for granted that one of the reasons a writer writes is that his article may be read. But he who starts his manuscript with colorless and leaden statements dampens at once the ardor of the would-be reader and may even turn him aside to seek more refreshing material elsewhere. How uninviting it is to read in the opening sentence that a given area is bounded by so and so and may be reached by such and such a route, when the point of interest to the reader is not so much the area as the problems of interest yielded by the area. It may be desirable to include the location and the route but its place is not in the beginning paragraph. Even supposing the reader's literary digestive apparatus is sufficiently hardy for him to gulp such unpalatable bits that he reads further to find what it is all about, then for him to be met by a page or so of production figures or bibliography or methods of field work or topography is unpardonable. He still wonders what it is all about. If the writer's purpose was to discourage the reader he has well-nigh accomplished his task.

On the other hand the carefully thought out introduction, which all literary work should have, allures the reader to investigate further. His attention once attracted, his interest is quickened and he is then unconsciously impelled to read. But how, you ask, may this be done? Scientific writing and literary style are not incompatible, notwithstanding the numerous examples to the contrary. If the article contains some points of interest, as most good papers do, why not mention them in the beginning, or at least give a suggestion of the problems conceived. And this need not and should not be a bald abstract. Should the writer fear a loss of effect upon the reader by stating his conclusions in the beginning, he at least can mention the problems dealt with, or the outstanding features of the article, in order that the reader early may know what the paper takes up. Incidentally, the title is not the place in which to do this. (Some of these remarks of course do not apply in cases where it is the custom of the writer to preface his article by abstracts or preliminary summaries.) Other less interesting, but neces-

sary material may then follow the introduction, and like a meat course following soup, the mental digestive tracts are pleasingly prepared for the more hearty substance to follow. And if in the opening paragraph the subject and problems be succinctly stated, and the writer adds here and there a word with a touch of color, the readability of the article will be increased no less than its literary quality.

Nor do I wish my indulgent reader to assume that these remarks are meant only for the other fellow.

ALAN M. BATEMAN.

DISCUSSION AND INFORMAL COMMUNICATIONS

THE CONTENT OF METALS IN INTRUSIVE MAGMAS

Sir: In the December 1923 issue of your journal J. F. Kemp calls attention to the fact that some mining districts produce several metals in commercial quantity, while others, such as the Mother Lode district in California, produce only one. From this circumstance he is led to propose the theory that in cases like the latter the original magma from which the ores originated contained only one of the commercial metals—in the case cited, gold—and hence "that, aside from iron, we have a one-metal magma." By contrast he cites Leadville, which has produced lead and zinc, silver and gold, and copper, as evidencing magmas containing several metals.

That different magmas are differently charged with metals, in a great variety of proportion, is indisputable, as is evidenced by the phenomena of metallographic provinces. I do not believe, however, that this selection goes so far that there are exclusively one-metal magmas, or even two-metal magmas. The Cornwall tin region is a metallographic province characterized by a notable primitive segregation of tin in the magma; yet there occur besides tin, copper, lead, zinc, and silver. The Sudbury nickel district is similarly a metallographic province characterized by a great primitive segregation of nickel; yet we have also copper, and also lesser veins of zinc and lead. The Mother Lode case with Professor Kemp cites does not, I believe, support his hypothesis. It is part of the auriferous vein region of the Sierra Nevada, whose veins originated in post-Jurassic time, subsequent to the intrusion of the extensive granodioritic magma of the Sierra Nevada. The gold veins of this metallogenic epoch and of this

metallographic province have the main characteristics in common, up and down the length of the Sierra Nevada. But besides the gold, there are copper deposits, less abundant, and of less importance, but probably of the same age and general magmatic affiliations, which have been considerably worked and fairly productive; so that Diller notes in 1905 that California stood fifth among the copper-producing states. One of the most important copper regions lies very near the Mother Lode, in a belt paralleling the lode, and only about 6 miles distant; but the magmatic affiliations of the copper are obscure, although Turner in the Jackson folio of the U. S. Geological Survey notes relations of certain of these copper mines to quartz-porphyrite intrusions, which quartz-porphyrite he lists as of the same general age as the granodiorite. For a clearer example of the relation of the copper ores to the gold ores, I may instance the copper (and gold) ores of Shasta County, a district which I have visited, and which is described by J. S. Diller in the Redding folio of the U. S. Geological Survey. Here are such once well known copper mines as Bully Hill and Balaklala. Diller states, "The fissures which gave access to mineral-bearing solutions, and thus permitted the formation of deposits of copper and auriferous quartz, originated chiefly during the epoch of rock making and mountain making about the close of the Jurassic. This is indicated by the fact that the fissures bearing ore have been found in the Jurassic rocks, but not in the Cretaceous." The gold occurs mainly in typical auriferous quartz veins; these are locally seen to be cut by the copper ores, which are chiefly chalcopyrite, with some blende and galena, gold and silver, and with much quartz and barite gangue.

The post-Jurassic granodioritic magma in this region is represented by intrusions described by Diller as granodiorite, quartz-hornblende diorite, quartz-mica diorite, and quartz-augite diorite. A study of Diller's folio suggests zonal arrangement around the main intrusive area (batholith) of quartz-hornblende diorite, the auriferous quartz veins mainly encircling the intrusion and sometimes lying in it, the copper ores lying further away from it.

These copper ores in the Sierra Nevada seem to fix the zone of the gold quartz veins as deeper than the copper zone; while numerous cases (among them Silver Peak) show the relative position of these same gold-quartz veins as also next above the zone of pegmatites and of pegmatitic quartz. (It is to be noted that in any region much of this pegmatitic quartz is barren, although auriferous quartz may occur higher up.) And we are therefore, perhaps, justified in the hypothesis that the zones above the copper zone—the zinc, lead and silver zones—have been removed by erosion, during the Cretaceous, Tertiary and Quaternary.

The depth which California veins have attained do not then, in my opinion, indicate a one-metal magma. The vertical extent of individual ore zones is clearly chiefly a function of relative change of temperature with increasing depth—of vertical spacing of the isogeotherms. This vertical spacing seems to widen in the lower zones of ore deposition, such as the zone of the gold-quartz veins, represented by the California types. So far we have no complete evidence as to how high (or deep) vertically this gold-quartz zone may attain.

I agree that development work based upon the zonal theory should be cautiously undertaken. Certainly this principle should never be applied to development work without the highest type of geological counsel. There are cases where the vertical spacing of zones has been within limits accessible to mining, and in such cases a carefully considered development plan may take the changes in depth into consideration. In many if not most cases, however, the complete investigation of changes in depth would involve sinking thousands, perhaps many thousands, of feet: and the practical limit for present-day mine exploration is soon exceeded. All mine development must be undertaken on a purely business basis.

Turning to a quite different subject, and away from the discussion with Professor Kemp, I wish to advise against calling the successive vertical zones of deposition metallogenetic zones, as has been done recently by two writers (R. H. Rastall and W.

Petrascheck) in ECONOMIC GEOLOGY. They are metallo-depositional zones, not metallo-genetic zones. The latter term has been used so widely and vaguely that it no longer has any clear connotation. Doubtless a definite term for these zones would be handy; but it must be a new term, to fit the new conception. Will someone propose an appropriate one?

NEW YORK, N. Y. J. E. SPURR.

NATURAL GAS IN THESSALY.

Sir: Emanations of natural gas have been reported recently in the basin of Trikkala in Thessaly, Greece, and have raised the question of the possibility of petroleum being found at this locality. The Trikkala is the western basin of the three that form the great Thessalian plain, and is surrounded by mountain ranges on three sides. On the eastern side the basin of Trikkala is not bounded by mountains, but a low range of hills separates it from the neighboring basin of Larissa. The basin is fertile and well populated, and is in communication with the capital and also with Volo, a flourishing port on the Pagaseticus gulf.

Topography.—The faintly undulating surface of the basin of Trikkala extends almost level to the foot of the surrounding mountains and hills. A few isolated hills of limestone interrupt here and there the monotony of the level plain. On the north rise abruptly the southern slopes of the Cambounia Mts., composed of crystalline schists and marbles. The slopes of the Pindus and Orthrys Mts., on the west and south, are more gradual. Numerous natural channels irrigate the basin and finally flow into the main river, Peneios, which drains the whole Thessalian plain. The surface of the whole basin appears to be composed of alluvial embankments, which have covered the deeper diluvial and Tertiary deposits.

Historical Geology.—The geologic history of the Thessalian basins is already known from the studies of Philippson[1] and Renz.[2]

[1] A. Philippson, "La tectonique de l'Egeide," *Ann. de Geograph.*, Tom. VII., p. 137. A. Philippson, "Zusammenhang der griechischen und Kleinasiatischen Faltengebirge," *Petermann's Mitt.*, 60 Jahrg., 1914, pp. 71–75.

[2] C. Renz, "Gebirgsbau Griechenlands," *Zeits. der deutsch. geol. Gesellschaft*, Monats. ber., 1912, 8–10, pp. 161–164.

The main folding of middle Tertiary age had already commenced when during the upper Oligocene or lower Miocene period an expanse of sea covered western Macedonia and Thessaly in a north-west direction, starting from the valley of the upper Aliakmon river and penetrating through Castoria and Grevena into the present basin of Trikkala, and spreading further through Pharsala as far as the Gulf of Volo.

After a period of deposition there followed a slight increase in the folding of the Pindus and Cotsiaka chains as an elevation of the whole district. In the upper Tertiary there was a period of great eruptions, accompanied by earth movements. This resulted in the creation of sea straits and gulfs, islands, inland seas, and plains. A wide basin was created in Thessaly, occupied by an inner lake. The deposits of this lake may be observed at the foot of the hills separating the basin of Trikkala from the lake of Larissa. Afterwards the bottom of the depression continued to sink so that the great original basin was separated in two parts. During this time the Peneios River widened its valley and the deposits of the lakes, which then occupied these two basins, were afterwards covered by the river embankments.

According to this, under the alluvial and diluvial embankments of the lake of Trikkala should lie the Tertiary deposits (Pliocene, Miocene, and Oligocene), which are found on the western slopes of the Agrafa and Chassia mountains, while still deeper are probably the lower Tertiary formations of the Pindus series.

Occurrence of Gas.—Emanations of natural gas have been noticed in three districts.

(*a*) Almandar. The first observation was made in a well sunk in 1920 to a depth of 40 m. We noted that from the water filled well came bubbles of inflammable gases of an empyreumatic odor. After pumping with an ordinary hand-pump for about a quarter of an hour, a more intense issue of gas commenced, and finally came an explosion of muddy water to a height of 4 to 5 m., and a large quantity of gas. This lasted from five to ten minutes, and gradually diminished, until only quiet bubbles arose.

(*b*) Palamas. Almost the same phenomenon was observed in a well at Palamas, drilled in 1920 to a depth of 75 m. According to the statement of the proprietor, limestone and sands were met with during the sinking of the well, and the gushing of gases started from a depth of 45 m. On our visit bubbles of inflammable gas rose continually and burned with a blue flame. After strong pumping the quantity of the gas became greater, amounting to 1 cubic meter in an hour.

(c) Molossi. The greatest gushing, however, occurs at Molossi from a well 40 m. deep. At 28 m. a small gushing started, which increased with the depth. At 36 m. a water-bearing stratum was met with, and a large quantity of gas was emitted. There was a continuous emission of gas to the amount of about 55 pounds per hour.

On our visit the well was pumped for thirty seconds, after which there was foam, a flow of muddy water, and then a lively emission of gases. The amount of gas diminished as follows:

9:45 A.M., 240 lbs. per hour
9:48 A.M., 210 lbs. per hour
9:50 A.M., 160 lbs. per hour
4:30 P.M., 72 lbs. per hour

After 24 hours from the time of pumping, the output reached that of the former day.

In all three wells no oily drops or traces of naphtha were observed in the water emitted with the gases.

Chemical Composition.—Three local analyses were made by means of Bunte's apparatus[3] on gas from the well at Molossi. The following average of three analyses gives the chemical composition of the gas.

2.2%	Carbon dioxide	36.2%	Hydrogen
0.4	Heavy hydrocarbons	33.0	Methane
0.3	Oxygen	27.3	Nitrogen
0.6	Carbon Monoxide		

[3] Analyses by M. Pertessis, chemist of the Geological Bureau, Ministry of National Economy, Greece.

Particularly noteworthy in the above chemical composition are the small percentage of heavy hydrocarbons, and the great percentage of methane and nitrogen.

Origin of the Gases.—If we classify natural gases in four categories,[4] *i.e.*, volcanic gases, gases enclosed in igneous rocks, coal and peat mine gases, and petroleum gases, the natural gases of Thessaly should be classified in the third category, according to their chemical composition. Gases from coal and peat mines contain as dominating elements methane and nitrogen, while those of the fourth category contain, besides methane, mixtures of other hydrocarbons, and nitrogen in comparatively small quantities.

At the time when the overland channel crossed through the basin of Trikkala, the Miocene beds of pitch-lignites were deposited, which are found in many places and are rich in volatile content. Also until recent geological time the Trikkala basin was occupied by a lake within which peat might be developed. It is therefore obvious to explain the origin of the natural gases as products of distillation of natural substances.

The chemical composition of the gases, the complete lack of traces of oil or naphtha in the waters issuing with the gases, and the almost complete disappearance of mineral hydrocarbons in the surrounding districts do not argue in favor of accepting these gases as oil gases.

G. C. GEORGALAS.

[4] *Cf.* J. Chautard, "Les gisements de pétrole," Paris, 1922.

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REVIEWS

Das Erdöl und seine Verwandten. By H. HÖFER-HEIMHALT. Vierte Auflage; Friedr. Vieweg & Sohn Akt.-Ges., Braunschweig, 1922.

In introducing to the readers of this magazine a new edition, the fourth, of a manual that has long been part of the working library of every petroleum geologist, the occasion permits reference only to departures from preceding editions, and more particularly the direction of attention to new views and new conclusions. Any new thoughts contributed by this patriarch in oil geology are bound to be of interest. There has been great activity in this branch of geology and much has been brought to light since the publication of the third edition in 1912, albeit the new material consists mainly of a splendid array of observations contributed by a host of ardent and trained geologists, rather than the discoveries of principles or the development of recent theories. Ours is a very young branch of geology.

The new edition contains about 30 pages and three illustrations more than the third edition, and part of the additional matter comprises mere enlargements of tables, lists, etc.; but type has been reset and not only has brief mention of many new items been incorporated, mainly by adding clauses or sentences to old paragraphs, but a considerable number of new paragraphs have been intercalated.

The matter relating to types of petroleum is rearranged and considerably revised, with the introduction of a discussion of regional alteration and its relations both to the qualities of oil and to its distribution. The relation between the advance in regional rock alteration, and the general advance in the grade of the oils to extinction at the regional carbonization limit, Höfer accepts, the lower rank and generally less saturated oils being regarded as primitive, the higher and more saturated, as more fully developed. A few definitions have been changed, greater prominence is given to the stratigraphy of oil, and very slight revision has been made of the history of oil development. However, in this part of the book practically nothing is added to the paragraphs published 10 years ago regarding South America,—Colombia, Peru and Argentina. Three new lines relate to Trinidad and Venezuela. The history of oil development in the "Western United States" is confined to California, except mere record of the discovery of the Jennings field in Oklahoma. Nothing is given of the remarkable progress during the last decade in east

Texas, the Mid-Continent region, Wyoming, or the less important States, beyond bare mention, under Eastern States, of the opening of the Gulf Coast oil fields through the discovery by Captain Lucas at Spindletop in 1901. A new section briefly considers the remarkable changes in Mexico during the last ten years, without mention of the failure of wells. Doubtless many of the omissions in this historical chapter are due to the restraint in transmission of scientific publications and thought during and consequent to the World War. The statement that I have forecasted that the oil production of the United States would continue for seventeen years only is, of course, the product of the journalistic mind, and can have reached Höfer only through that medium. That a geologist knowing anything about the life of American oil fields should appear to accept the statement and quote it without verification or question is inexplicable. For the growth of production in the States, figures later than 1908 are not given in this chapter.

The chapter on the physical characters of oils has been subjected to slight revision with minor changes regarding viscosity and absorption, and cognizance is taken of the important evaporation investigations of the U. S. Bureau of Mines. A new section on solidification is introduced and the section on emulsions and solutions is revised to take account of recent progress of discovery. The tables and graphs showing densities and viscosities of oils in the different countries remain unchanged.

In the chapter on the chemical constituents of bitumens the formation of asphaltenes in the California oil fields is attributed to the action of the connate water in the same beds. No mention is made of the helium in the natural gases of Texas, Oklahoma, and Kansas. The great progress during the last ten years in the extraction of gasoline from natural gas is reflected by extensive revision of that part of the book, which now includes helpful reference tables to show dryness or wetness of gases in the principal oil regions of the world.

The most important contributions for which this distinguished oil geologist is known throughout the world relate to the mode of origin of oil, and to the conditions of its occurrence, and the chapters on these subjects are, consequently, of greatest interest to the American reader. The latter finds, however, little that is both new and important on either subject. As in previous editions, Höfer contends with zealous pertinacity for the theory of the animal origin of oil and for its origin nearly everywhere in the very beds where it is now found. Migration across the bedding he sees as absolutely impossible except along joints and fissures, notwithstanding the obvious facts that water and other fluids have moved upward out of even the densest and finest-grained clays and other sediments in the process of dehydration under depositional loading long be-

fore joints and fissures were formed, and that the volatile matter passing out of carbonaceous clays, etc., must travel a measurable distance to reach the nearest joint or cleavage plane. Secondary deposition he concludes must be extremely rare, though he more readily concedes lateral migration in the same bed. Capillary influence on oil movement as urged by Washburne and McCoy receives scant treatment, with obvious minimization and dismissal.

The most prominent change in this part of the book is the introduction of a new chapter on the geotectonics of oil, to take the place of a part of the old discussion under the caption "Oil lines." Here his rather murky claims for credit as the originator of the anticlinal theory remind one of recent European diplomacy as to oil concessions. In his discussion of regional carbonization and oil occurrence Höfer assumes that the oil-bearing formations have endured the greatest pressure, and so been, presumably, most compressed where they are more strongly folded, quite ignoring the fact that in many areas beds held in position by competent formations must have endured greater lateral thrust and suffered greater consequent compression than those in areas where less competency has permitted buckling and overthrust with resultant relief at less intensity of stress. Königsberger's conclusions as to the existence of high geothermal gradients in oil fields are adopted as due to chemical reaction in the bitumens.

In the discussion of the origin of oil there are new paragraphs dealing with some of the literature later than 1911, but little that is new in conclusions or point of view. For, while in reviewing certain investigations of oil shales or recent deposits of fatty, oil-producing algæ Höfer each time concedes the "possibility" that such fatty or waxy plants may with limitations, have taken part in oil formation, succeeding paragraphs, unchanged from earlier editions, contend for an origin exclusively from animal matter. Even in his revised statement of theory there is but the scantiest recognition of possible participation by any plants in oil generation. On the other hand, his objections to the views of the newer plant advocates are sometimes shifty. He gives equal attention to carbohydrate plants and impressions of leaves, on the one hand, and sapropelic or "fatty" algal material, on the other. Much of this chapter that is given to citations and rebuttal of early and middle period literature concerning the woody plants might well have been abridged or even eliminated from the book as dead issues. To Höfer's mind sapropelic matter, even the purest alga boghead, seems to owe its virtue to the unseen animals that must have been preserved, in the fat if not in the flesh, in the buried strata. In his arguments and assumptions that the bituminous shales in the areas under consideration are sources of petroleum only through their animal contents, he gives no thought to the abundance of

waxy, fatty and resinous plant material in the shales, which may never have been examined with the microscope, and concerning the microscopical constitution of which he shows little interest and less faith. The recent surprising disclosures of innumerable waxy or fatty algæ in bituminous shales, as well as bogheads, and in deposits now forming in certain regions of the world, and the chemical and distillation tests of these deposits, evidently have made little impression on Höfer. He falls back on his old arguments, familiar to all oil geologists, viz.: Plants leave carbonaceous residues, animals do not; there are no carbonaceous residues in the sands which contain the oil and in which the oil originated from animal matter. Höfer should consider Florence, Colorado. The microscope is a great educator respecting the origin of the bituminous sediments, as well as the vestigial residues in oil sands, and, supplemented by micro-chemistry, both of fossil and recent deposits, promises to throw great light on the origin of oil, in which it may be seen that the part played by plant life of some lower orders may, to say the least, be not less important or widespread than that of animals.

If the fourth edition of "Das Erdöl" is not all that it might be, it is nevertheless a most valuable and indispensable member of a geologic reference library. An interesting feature of the chapter on the search for oil pools is Höfer's recommendation of the Eötvös gravity balance, for use in locating anticlines and domes.

DAVID WHITE.

Report on the Cupriferous Deposits of Cyprus. By C. GILBERT CULLIS AND A. BROUGHTON EDGE. London, 1922. Published by the Crown Agents for the Colonies, 4, Millbank, London, S. W. 1. Price 20 shillings.

Although in Phœnician and Roman times the island of Cyprus was so noted as a source of copper that the name of the metal was derived from the name of the island, until recently no mining had been done for many centuries. Large accumulations of slag near certain gossan-capped hills bear witness to the ancient industry but few traces of the old workings remain and up to the year 1914 nothing was known of the existence of any ore body of sufficient size to justify modern operations. In July of that year an American syndicate, while carrying out systematic drilling discovered a large body of pyritic copper ore near Skouriotissa, on the north side of the island, near its western end. Subsequent underground development revealed a system of ancient workings, showing that the Skouriotissa deposit was one of the sources of copper for the ancient world.

Cyprus has an anticlinal backbone of massive limestones and dolomites,

which in places have been converted to marble. The total thickness of these sharply folded rocks is estimated at from 5,000 to 6,000 feet and, although poorly provided with fossils, the beds are considered to be Cretaceous. These rocks are overlain by the Kythrean series of sandstones, shales, conglomerates and marls, believed to be upper Eocene or Oligocene in age. Resting upon the Kythrean series is the Idalian series of Miocene age, which is the surface rock over nearly half of the island. At the base of this series is about 400 feet of argillaceous gray or greenish marl with layers of gypsum. This division is succeeded by from 1,200 to 1,500 feet of snow-white chalk and chalky marl with layers of flint and chert. The topmost member consists of roughly bedded cream-colored shelly and coralline limestone. The island also contains calcareous beds of Pliocene age, from 250 to 350 feet in total thickness, and unconsolidated Quaternary deposits.

The igneous rocks are predominantly basic and ultra-basic although some intermediate and siliceous types are represented. They occur chiefly in the Troödos Range in the southwestern part of the island. The intrusive rocks include diabase and serpentine, the latter an altered peridotite and associated with masses of gabbro and other basic rocks. These rocks invade all of the sedimentary formations older than the Pliocene. The effusive rocks, which are closely associated with the intrusive rocks are more or less altered basaltic rocks of the type known as pillow-lavas. Whether these lavas are older or younger than the diabase and serpentine has not been definitely ascertained. The pillow-lavas rest generally on the diabase and are overlain by the marls of the Idalian series. The authors believe that the pillow-lavas are younger than the diabase and were poured over a sea bottom during the period of depression in which the Idalian marls were deposited.

Copper ores occur in two modes: (1) in fissure zones in the diabase and (2) as irregularly lenticular, flat-lying masses between the pillow-lava and the overlying Idalian marl.

The deposits of the first class grade into the unmineralized diabase. The principal sulfide is chalcopyrite, generally dispersed through the shattered rock and in places accompanied by pyrite. Where oxidized, this material is conspicuously colored by copper carbonates and may contain cuprite and native copper. None of these deposits, so far as known, is of economic character.

The deposits of the second class consist chiefly of pyrite and carry up to about two and one half per cent. of copper. Chalcopyrite is probably generally present but is rarely visible. The ore is essentially a sulfur ore containing copper as a by-product, and resembles the cupriferous pyritic ores of Norway and southern Spain.

The typical ore body is a lenticular mass, which may cover a dome on

the pillow-lava or may lie in a depression in that lava. It is covered by the Idalian marl which for a few feet above the ore has been changed to a dark brown umber. The maximum thickness of the ore appears to be about one hundred feet. Similar but smaller lenticular masses of ore may occur in the pillow-lava some distance below the contact and under the ore bodies the lava may show nearly vertical zones of mineralized rock which are interpreted as marking the channels up which the ore-bearing solutions rose.

The authors conclude that the ore bodies were formed by the damming or checking of iron, copper, and sulfur-bearing solutions which rose through the fissured lava and spread out at the base of the marl. These solutions are believed to have been generated shortly after the eruption of the lava as a manifestation of solfataric activity. They reacted with the rock of the upper part of the lava formation and produced low-grade disseminated pyritic deposits. At the contact the replacement was more nearly complete and the massive sulfide ore was formed.

So many of the large copper deposits that have been opened in recent years are associated with granitic or monzonitic intrusive rocks as to give a rather overwhelming importance to those types of igneous rock as sources of copper-bearing solutions. It is consequently of interest to find in this work a careful description of pyritic copper ore which appears to be genetically connected with the eruption of basaltic or diabasic magma. The Skouriotissa type of deposit is in several respects a remarkable one and it is to be hoped that, with the progress of mining, further investigation concerning its origin will be carried on. It is worthy of note that the ore from which so much of the copper of the ancients appears to have been won is a low-grade sulphide which must have required enormous labor to mine and no mean metallurgical ability to treat.

F. L. RANSOME.

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SOCIETY OF ECONOMIC GEOLOGISTS

The following officers have been elected for 1924:

James F. Kemp, President,
Edson S. Bastin, Vice President,

and the following Councilors, to serve until December, 1925:

George H. Ashley, D. F. Hewett.

The other members of the Council are:

Ralph Arnold, L. C. Graton, Willet G. Miller.

The following were elected to membership in the Society on the December 15th ballot:

Axel Gavelin,
John Alden Grimes,
Percy Eugene Hopkins,
Frank J. Katz,
Mack Clayton Lake,
Wilbur Armistead Nelson,
Mark Newman,
Orrin P. Peterson,
John A. Reid,
Max Roesler,
Stuart J. Schofield,
Ransom Evarts Somers,
Douglas G. H. Wright.

The results of the Secondary Enrichment Investigation conducted by Professor L. C. Graton and associates will be presented at a joint meeting of the American Institute of Mining and Metallurgical Engineers and the Society of Economic Geologists, to be held at the time of the annual meeting of the latter at the United Engineering Building, 29 West 39th Street, New York City.

On December 29, 1923, the Society held a business meeting at the Cosmos Club, Washington, D. C., preceded by a luncheon. Some 46 members attended and the discussions regarding meetings, publications, and bibliography were general.

SCIENTIFIC NOTES AND NEWS

Joseph T. Singewald, Jr., professor of economic geology at the Johns Hopkins University, and Lincoln Ellsworth, of New York, will sail for Peru in February to carry on some geologic explorations in the Andes of central Peru, and later the collections will be worked up at Johns Hopkins. The expedition will be known as the Ellsworth Expedition.

Percy E. Hopkins has resigned his position with the Ontario Department of Mines to enter the service of the Mond Nickel Company.

J. E. Spurr has been invited to lecture on ore magmas, or in general on the origin of ores, by the University of Wisconsin, which each year invites some outside man for a series of three lectures on some special topic of interest. Mr. Spurr has also been invited by Johns Hopkins University to deliver a series of five lectures on the same subject.

Kirk Bryan returned to the U. S. Geological Survey in January after making extended investigations for water supplies in Washington.

During the absence of Professor Joseph T. Singewald from Johns Hopkins University for the spring term, his work will be carried on for him by a number of the members of the U. S. Geological Survey, each giving lectures for a brief period.

Frederick G. Clapp is temporarily absent from this country on professional work in Australia.

Arthur Notman, former mine superintendent of the Copper Queen Mine at Bisbee, and J. R. Finley, of New York, have returned from their examination of mining property near Nacozari, Mexico.

H. A. C. Jenison has resigned from the U. S. Geological Survey and has accepted an appointment with the Senate Gold and Silver Inquiry Commission.

W. F. Holmes, Secretary for Mines in the Gold Coast Colony and Ashanti, is now at the Mine Department, Tarquah, Gold Coast Colony.

B. R. Mackay has been appointed geologist on the Canadian Geological Survey to work on an investigation of coal deposits in collaboration with Dr. D. B. Dowling.

Howland Bancroft has resigned from the Sinclair Consolidated Oil Corporation and is spending the winter in Denver.

S. C. Ells of the Canadian Department of Mines has completed a survey of the tar sands along the Athabaska River in Alberta, having mapped out an area of about 1200 square miles.

Charles T. Kirk, of Tulsa, spent the month of November in the examination of silver prospects in the state of Oaxaca, Mexico. He finds that the ore provinces of that region resemble those of the Andes rather than the Rockies, particularly in the general absence of barren quartz float.

Another Emmons Memorial Fellowship in Economic Geology will be awarded for the next academic year. The holder of the fellowship will receive about $1,000 and is expected to carry on some worthy investigation in Economic Geology. Application blanks may be obtained from the Secretary of Columbia University, New York City, and must be filled out and submitted to the Committee on Awards, consisting of Professors J. F. Kemp, Waldemar Lindgren, and Alan M. Bateman, before March 1.

The ninth annual meeting of the American Association of Petroleum Geologists will be held at Houston, Texas, March 27th, 28th, and 29th, 1924. All members of the Houston Geological Society are giving their hearty coöperation to this end and will present an addition to Gulf Coast Geology in the form of a monograph on salt domes.

Two sessions are allotted for the discussion of salt domes and a few of the more important fields will be thoroughly described and discussed. The time allotted is not sufficient to permit the reading of all salt dome papers, but every dome in Texas and Louisiana will be described in detail and published in the bulletin, together with a map showing topography, stratigraphy, cross-sections, and development. Mr. E. DeGolyer will present a paper on "The Origin of Salt Domes."

A number of field trips will be made to some of the more important domes to show the visiting members what a salt dome looks like, its surface indications, and their relation to production. The inside of a dome will also be inspected at Averys Island, La., as well as methods employed in mining sulphur at Freeport, Texas. These trips will offer an opportunity to study rotary methods and the problems peculiar to salt dome structures. The trips are:

March 28th—Automobile trip to Barbers Hill and Goose Creek Oil Fields;
March 30th—Special Train to Freeport Sulphur Mine and Hoskins Mound;
March 31st—Trip by Southern Pacific R. R. to Averys Island, La.;
April 1st—Final trip to Palestine visiting two or three of the inland domes.

The Geological Society of America held its thirty-sixth annual meeting at Washington, D. C., December 27–29, and it was the best attended meeting ever held by the society. More care than usual was exercised in the selection of papers. Each paper was assigned a definite time and the Council are to be congratulated that this schedule was so rigidly adhered to. It is perhaps to be regretted that the schedule did not allow more time for discussion and that many interesting discussions had to be stopped just as they were well under way. Fewer simultaneous sessions than usual were held, consequently each member had greater opportunity to listen to the papers of his choice. The affiliated Paleontological and Mineralogical Societies and the Society of Economic Geologists met at the same time, though the Society of Economic Geologists did not hold a technical program. An outstanding feature of the meeting was the Annual Dinner at which the Pick and Hammer Club staged a play supported by their chorus. Several members of the Society were the butt of their playful and clever jests. A dance followed. It was a new and pleasing innovation for the Annual Dinner and the Washington members are to be congratulated for its success.

Among the papers listed that dealt with economic geology are: Bauxite Associated with Siderite, by E. F. Burchard; Dolomitization in Southern Nevada, by D. F. Hewett; Sulphate Minerals Formed by Oxidation of Pyritic Ore at Bisbee, Arizona, by H. E. Merwin, Augustus Locke, and E. Posnjak; Primary Native Silver Ores of South Lorraine, by E. S. Bastin; Paragenesis of the Bolivian Silver Tin Ores, by G. M. Hall; Native Copper in an Iron Mine, by A. C. Lane; X-rays and Crystal Structure, by A. F. Rogers and P. F. Kerr; The Reaction of Cupric Salts in Aqueous Solution on Chalcocite above 200°, by R. C. Wells.

The Field Museum of Natural History, Chicago, has started to bring out leaflets in regard to displays of interest in their museum. Copies of the leaflets may be obtained from the museum. The publications thus far issued are as follows:

1. Model of an Arizona Gold Mine, by Henry W. Nichols. 12 pp., 1 plate. This leaflet describes a mine model, made to demonstrate the ordinary features of mines and methods of work, and explains the main features of an ordinary mine, with definitions of technical terms.

2. Models of Blast Furnaces for Smelting Iron, by Henry W. Nichols. 10 pp., 3 plates.

3. Amber—Its Physical Properties and Geological Occurrence, by Oliver C. Farrington. 7 pp., 3 plates. Intended to supplement a collection of Baltic Sea amber, this leaflet tells what amber is, how it was formed, how it is gathered, and something of its varieties.

4. Meteorites, by Oliver C. Farrington. 11 pp., 4 plates. This leaflet, based upon a study of the Museum meteorite collection, is an account in

readable form of facts of general interest concerning meteorites; their appearance, composition, and the phenomena which accompany their fall, as well as the theories of their origin.

The Twenty-sixth Annual and General Meeting of the Canadian Institute of Mining and Metallurgy will be held in Toronto, on the 5th, 6th, and 7th of March, 1924. The special subject under discussion this year will be opportunities for mining investments in Canada, and papers on other subjects of general interest will also be presented.

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